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Chromium Contamination in the Glasgow Environment and the Potential for Remediation

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In the Name of Allah, the Most Compassionate, the Most Merciful

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Declaration

This thesis and the research described here are performed entirely by the author except where expressly stated.

Basmah G. AL-hogbi

Summary

Recently, concern about chromium as an environmental pollutant has been escalating due to its build up to toxic levels in the environment as a result of various industrial activities. Chromium often occurs in the trivalent (III, chromic) or hexavalent (VI, chromate) states under natural environmental conditions. The hexavalent state of chromium, Cr (VI), is highly toxic and carcinogenic. The high aqueous solubility of Cr (VI) is of public health concern since the anionic forms, chromate and dichromate, are considered hazardous. The trivalent state of chromium, Cr (III), is much less toxic than Cr (VI) and relatively insoluble.

Rutherglen in South-East Glasgow has a significant concentration of chromium in the environment arising from waste dumped in this area from a former chromium works, which operated for about 140 years up to 1968. In this dumpsite area the total chromium concentration measured by aqua regia digestion was (2000-10,000 mg/kg), and the water extracted chromium was entirely Cr (VI), in the range of (10-1200 mg/kg), which is known to be toxic and carcinogenic. Total chromium (Cr (III) + Cr (VI)) was measured by atomic absorption spectrometry; Cr (VI) was measured by colorimetry. Soils sampled in southeast Glasgow local to the contaminated area suggest a background of 60 mg Cr/kg. In soil samples from northwest Glasgow transect, away from the dumpsite, the mean chromium concentration was about 30 mg/kg, which could be evidence of wind blow affecting southeastern Glasgow. There is evidence from the literature that chromium has started to leach from the dumpsite to the groundwater. Chromium released into the air, water, and soil can be transported among the various environmental media through various intermediate transport processes. Since the last decade attention has been focused on the

suitable remediation strategies for wind spread and leaching of hexavalent chromium to remove Cr (VI) or reduce it to Cr (III), which is less toxic.

This project investigated the traditional treatment of chromium by oxidation-reduction reaction using Fe (II) and Mn (II). It was found that Fe (II) was a potential remediation to stabilise chromium and reduce Cr (VI) to Cr (III), but Mn (II) oxidised Cr (III) to Cr (VI) mobilising it to the leachate.

The characteristic of chromium leaching from soil was studied and showed there was fast release followed by a slow release. After a dry period the initial leachate had a high chromium concentration, this points out that the leaching of chromium is a long- term process. Those aspects of fast and slow release and the high chromium concentration at the initial pulse have been a concern for designing a system of fixed bed, low cost material such as (charcoal, coir, peat and wood bark) for adsorbing chromium from the leachate.

The adsorption – desorption properties were studied, as both are of equal concern, and the Langmuir equation was applied for the various sorbent materials. Charcoal had a high percentage of Cr (VI) adsorbed, but on the other hand also had a high percentage of Cr (VI) desorbed. When applied to the column leach charcoal could not adsorb Cr (VI) properly. Wood bark had the lowest percentage of chromium released to the solution; therefore it was selected for further studies. The wood bark was studied with different contact times by both batch and flow through systems. The results showed that more chromium was adsorbed with longer contact time. The system using 2500g of wood bark completely retained chromium from a solution of about 100 litres of 30 mg Cr/l with a flow rate 60 ml/h. The experimental results can be applied to larger scale systems, however the system needs further development.

Table of Contents

List of Tables

List of Figures

Chapter 1

Introduction

1.1. The chemistry of chromium

Chromium in the Periodic Table is a d-block transition metal of Group VIB. It has an atomic number of 24 and an atomic weight of 51.996; of the five known isotopes the most common is 51Cr (half-life 27.8 days). Chromium metal is gray and brittle and can be highly polished (McGrath, 1995).

Chromium has different valence states ranging from Cr (0) to Cr (VI) with different stability, most common oxidation numbers (0) (elemental), (III) and (VI). The trivalent and hexavalent states are the most stable and the most important forms in the environment. The classified chemical species of chromium in the environment and their occurrences in nature are summarized in Table (1.1).

Table 1-1 Chemical species of Chromium (Nieboer and Jusys, 1988); (Zayed and Terry, 2003)

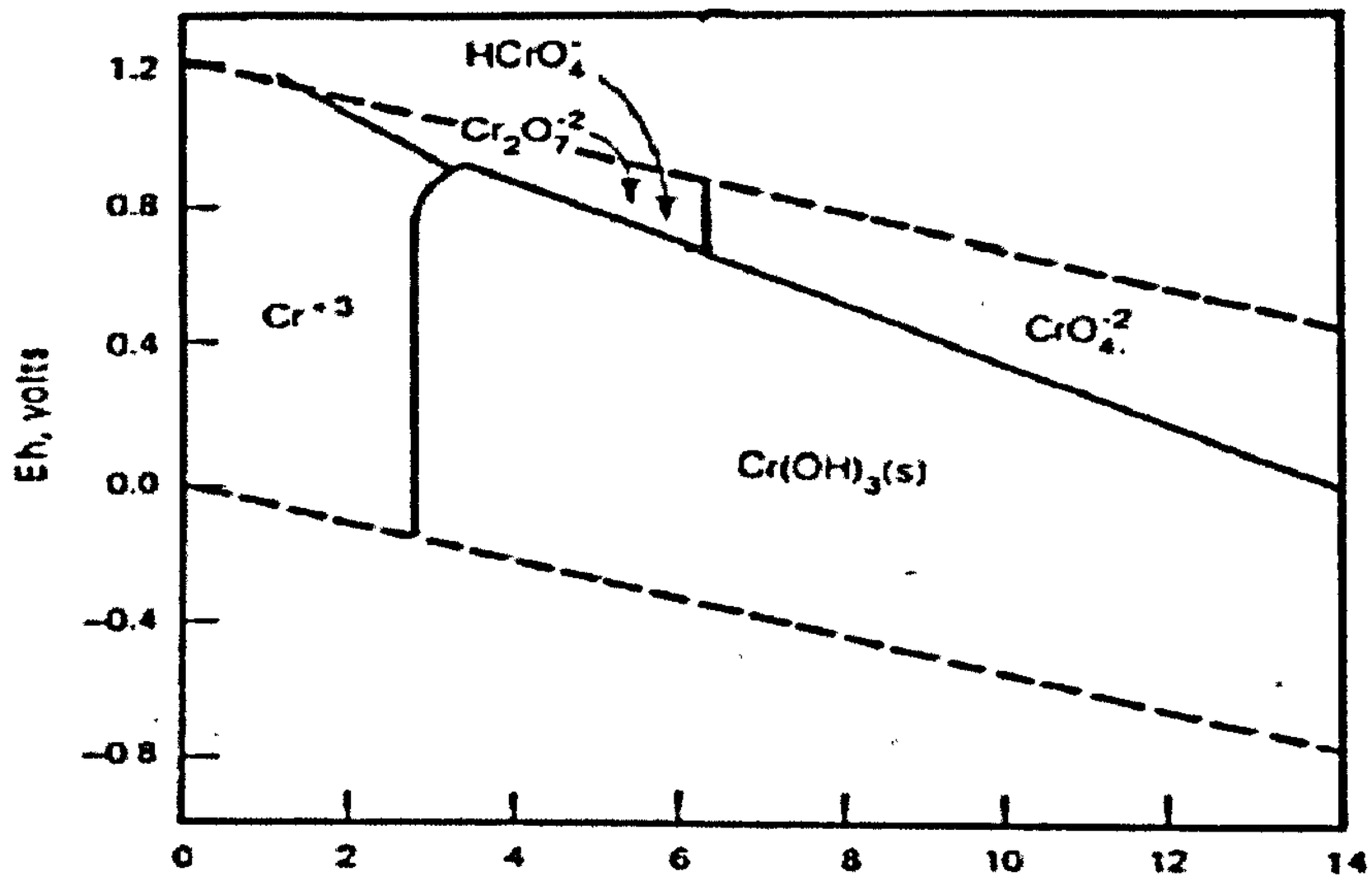
Chemical species	Oxidation state	Examples	Remarks
Elemental Cr	Cr (0)		Does not occur naturally
Divalent Cr	Cr(II)	$CrBr_2$, $CrCl_2$, CrF_2.	Relatively unstable and is readily oxidized to the trivalent state
Trivalent Cr	Cr (III)	$CrCl_3$, Cr_2O_3, $Cr(H_2O)_6^{3+}$	Forms stable compounds and occur in nature in ores, such as ferrochromite ($FeCr_2O_4$).
Tetravalent Cr	Cr (IV)	CrO_2	Does not occur naturally and represents an important intermediate that influence the rate of reduction of the Cr (V) form. Cr (IV) compounds are less common. The Cr (IV) ion and its compounds are not very stable and because of short half-lives, defy detection as reaction intermediates between Cr (VI) and Cr (III).
Pentavalent Cr	Cr (V)		Does not occur naturally and represents an important intermediate that influence the rate of reduction of the Cr (VI) form. Cr (V) species are derived from the anion CrO_4^{3-} and are long-lived enough to be observed directly. However, there are relatively few stable compounds containing Cr (V).
Hexavalent Cr	Cr (VI)	CrO_3, CrO_4^{2-}, $Cr_2O_7^{2-}$	The second most stable state of Cr. However, Cr (VI) rarely occurs naturally, but is produced from anthropogenic sources. It occurs naturally in the rare mineral crocoite ($PbCrO_4$)

The environmental chemistry of chromium compounds involves oxidation-reduction transformations, precipitation-solubilization reactions and adsorption-desorption phenomena (Katz and Salem, 1994).

In the environment, chromium occurs only in (III) and (VI) oxidation states, with Cr (III) being the most stable form. The ionic radii are 0.052 - 0.053 nm for Cr (VI) and 0.064 nm for Cr (III) (Bartlett and James, 1988; McGrath, 1995).

Figure 1.1 illustrates the Eh – pH diagram for chromium. It provides a generalized representation of the dominant aqueous species and their stability under varying redox and pH in chemical equilibrium conditions. In the natural environmental or soil system chromium may undergo changes in oxidation state if the redox condition of the soil or environmental is altered (Rai et al., 1989).

Oxidized



Reduced

pH

Acid Alkaline

Figure 1-1 Eh-pH diagram for the various chromium species (Rai et al., 1989).

Chromium (III) is the most stable form. From Figure 1.1, Cr (III) precipitates as Cr $(OH)_3$ above pH 3 under oxidising conditions. The hydrated Cr (III) ions, Cr $(OH_2)_6^{3+}$, can hydrolyze with release of proton. In very acid condition, Cr $(OH_2)_6^{3+}$ dominates, while at pH 4 about 50 % of the ionic species is Cr $(OH_2)_5 OH^{2+}$.

Chromium (VI) is strongly oxidized and best known in the form of chromate, CrO_4^{2-}, and dichromate, $Cr_2O_7^{2-}$, which are well known and widely used. In water solution, they exist in equilibrium with each other Equation (1.1) (Parker, 1993).

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+ \qquad \text{Equation 1-1}$$

Different species can be found at different pH. H_2CrO_4 is strong acid (pK= -0.6) and is the main species at low pH (Figure1.1). The orange dichromate is predominant in acid solution and is a strong oxidant Equation (1.2) (Nieboer and Jusys, 1988).

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^0 = 1.35V \qquad \text{Equation 1-2}$$

By contrast, $HCrO_4^-$ is a weak acid (pK= 5.9) and is the primary species at pH higher than pH 1, the yellow chromate ion dominates in basic solutions at high pH (Figure1.1), and is much less oxidising Equation (1.3) (Nieboer and Jusys, 1988).

$$CrO_4^{2-} + 4H_2O + 3e^- \rightleftharpoons Cr(OH)_3(s) + 5OH^- \qquad E^0 = -0.13V \qquad \text{Equation 1-3}$$

Chromate and dichromate ions form many soluble salts, which represent the mobile and potentially toxic forms in water. Under anaerobic conditions, these species are rapidly reduced to Cr (III) and precipitated as hydroxides and oxides.

1.2. The Toxicity of Chromium

Chromium is recognized both as an essential nutrient and as a carcinogen, depending on the oxidation state and solubility. Chromium (III) is an essential element for humans and other animals, it is an important component of a balanced human and animal diet and its deficiency causes disturbance to the metabolism of glucose and lipids.

In contrast, hexavalent Cr (VI) is highly toxic and may cause death to animals and humans if ingested in large doses. It is more corrosive than the trivalent form. Chromium (VI) is a known human carcinogen via inhalation and ingestion, attacking the lungs, stomach and nasal cavity. In addition chromium (VI) has been shown to have mutagenic potential (Syracuse Research Corporation, 1993).

Tests on animals show that the LD_{50} (i.e. the concentration causing a 50 % death rate) is 3,000 mg/kg for trivalent chromium and 80 mg/kg for the hexavalent form according to the U.S. National Institute for occupational Safety and Health (NISOH) (Katz and Salem, 1994; Registry of Toxic Efficts of Chemical Substances, 1986). The workplace exposure limit (WEL) is a measure of the concentration of a substance in the air over an eight hours period (ie. the average working day). For trivalent chromium the WEL has been set at 0.5 mg/m^3 compared to just 0.05 mg/m^3 for the hexavalent form. The recommended Estimated Safe and Adequate Daily Dietary Intake (ESADDI) of Cr is 10 - 40 μg/day for infants up to 6 months old and 50 - 200 μg/day for adult and children 7 years and older (DEFRA, 2002a). Because of the difficulties in characterising the oxidation state of chromium in an environmental sample, it is recommended that as a starting point in the absence of further information to the contrary, this ESADDI is applied to all the chromium content of an environmental sample.

Chromium containing substances of various chemical composition and chromium oxidation states have been shown to cause sensitisation, or to produce reactions (skin or respiratory effects) in already sensitised people. The ultimate allergen is believed to be a chromium (III)- protein complex, but it is the chromium (VI) compounds that most readily produce sensitisation because of their ability to cross biological barriers and subsequently to be reduced to the trivalent form (DEFRA, 2002c).

Chromium (VI) is rated as more phytotoxic. Critical concentration of Cr in plants is in the range 5 - 30 mg/kg (Alloway, 1995), but generally concentrations in plant tissues are <1 mg/kg (Alloway, 1995; McGrath, 1995). Biological function and level of chromium toxicity is more important to animals than to plants, but the most insidious hazard to human health is because the elements may accumulate in apparently healthy plants to levels that are poisonous to humans and animals (McBride, 1994).

1.3. Chromium in soil

1.3.1. Natural occurrence

Chromium is the 21st most abundant element in the crustal rocks, with an average concentration of 100 mg/kg rock.

Table 1-2 Concentration of chromium in various types of rock (mg/kg) (Ross, 1994).

Type of rocks	Cr mg/kg
Ultramafic	1000-3000
Mafic	200
Granite	4
Limestone	10
Sandstone	35
Shale	100

Chromium in igneous and sedimentary rocks table (1.2) readily substitutes for Fe, which has an ionic radius of 0.067 nm, close to that of Cr (III). Mafic and ultramafic rocks are richest in Cr, containing approximately up to 3000 mg/kg of Cr in chromites, which is a spinel also known as 'chrome iron ore'. Chromite is associated with mafic and ultramafic rocks. The composition of the ores varies between 42 – 56 % Cr_2O_3 and 10 - 26 % FeO, together with varying amounts of MgO, Al_2O_3 and SiO_2. Three types of ores are recognised, according to end use (McGrath, 1995).

1. Metallurgical, which has a minimum of 48 % Cr_2O_3 and a Cr: Fe ratio of 3:1.
2. Refractory, which must have high Cr_2O_3 and Al_2O_3 but low Fe.
3. Chemical, with high Cr_2O_3 but low SiO_2 and Al_2O_3.

Chromium (III) also replaces $Fe^{3+}$and Al^{3+}in many other minerals, resulting in Cr tourmalines, garnets, micas and chlorites. Traces amounts of Cr give color to other minerals e.g. the green of emerald and red of ruby (due to chromic oxide).

1.3.2. Inputs to soil

Chromium is one of the key metals whose use is nurtured by our modern technological society. Between 1950 and 1980, Figure (1.2) shows that the historical production of chromium increased at a sharp but steady rate of about 10 % per year (Nriagu and Nieboer, 1988).

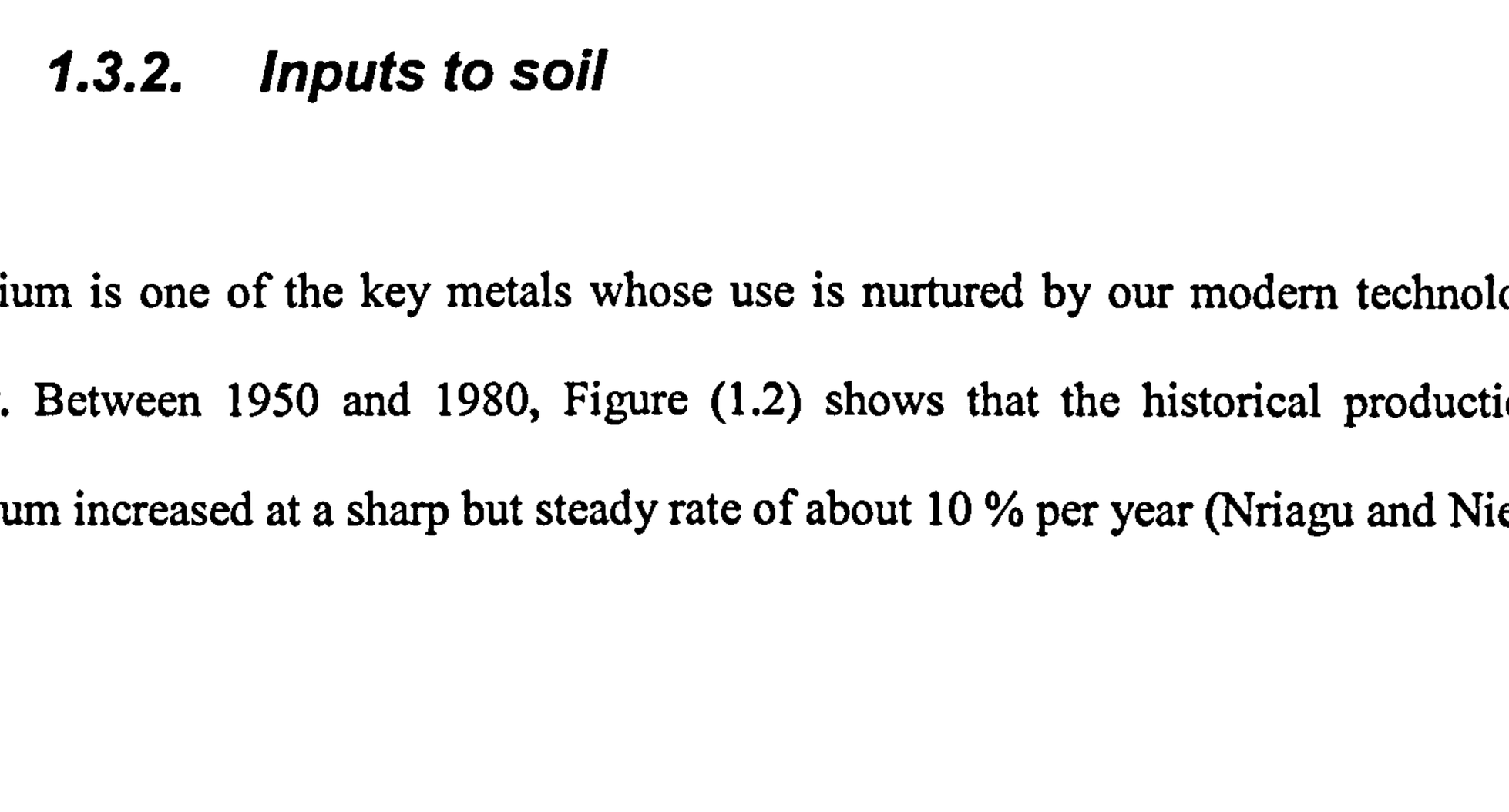


Figure 1-2 Historical trends in the worldwide production of chromium

1.3.2.1. Agricultural materials

The total annual input of Cr into soils worldwide has been estimated to be between 480 - 1300 x 10^5 t (McGrath, 1995). It is clear that soils are gaining much larger amounts of chromium than the other environmental media: 142,000 t/y for water and 30,000 t/y for air emissions (Nriagu and Nieboer, 1988) Fertilisers contain Cr, with phosphates being the richest in Cr. The Environmental Protection of Canada Ottawa (1976) reported a range of 30 - 3000 mg Cr/kg in phosphate fertilisers. Although the amount of Cr entering soil via use of phosphate fertilisers is uncertain, it is likely to exist as Cr (III) in soil and, as such, is not likely to be toxic.

Chromium is not used in agricultural pesticides, but limestone used to correct soil acidity contains Cr. Published values vary: <1 - 120 mg Cr/kg limestone rock, average 10 mg/kg (Environmental Protection Canadian, 1976).

Therefore, it is unlikely that there will be a large build-up of Cr in the soil as a result of application of most fertilisers and agricultural wastes.

1.3.2.2. Sewage sludge

Metals from natural, domestic and industrial sources concentrate in the organic residue at sewage treatment works. Chromium containing effluents are released by the following industrial activities, including metallurgical, metal plating of refractory bricks for lining furnaces, pigments for paint, tanning as an agent for leather and dyes, wood preserving, textiles, anodising and corrosion inhibitors in cooling water, ink manufacture, Cr chemical production, glass, ceramics, glues and coating for video/audio tapes (Zayed and Terry, 2003).

Both Cr (III) and Cr (VI) can be present in these wastewaters. However, many effluents are either treated on site to decrease the potentially toxic load in wastewater or sewage treatment works, where Cr (VI) is reduced by organic matter and consequently the Cr in sludge exhibit the chemistry of Cr (III) compounds (McGrath and Loveland, 1992). Removal of Cr from wastewater by sludge depends on the process used and the age of the sludge. In experimental continuous flow systems, using activated sludge, (McGrath, 1995) regarded that nearly 100 % of Cr (III) was removed, mainly by precipitation.

Many countries now adjust the quantity of metals that can be applied to soils in sewage sludge or have maximum metal concentrations in the soil itself. The presence of industries such as tanneries and plating works explains the upper concentration of Cr reported in sewage sludge from England and Wales the mean concentration of chromium in 193 samples is 335 mg/kg (McGrath and Loveland, 1992). In sludge farms, which had routinely received sludge from a treatment works for many years concentrations of Cr in surface soils (531-2020 mg/kg) (McGrath and Loveland, 1992). Very high levels of Cr (VI) contamination (14600 mg/kg in ground water and 25900 mg/kg in soil) have been reported in 27 Superfund sites in the USA (Krishnamurthy and Wlikens, 1994).

Chandra, et al., (1997) estimated that in India alone about 2000 to 3200 t of elemental chromium escape into the environment annually from the industries, with a Cr concentration ranging between 2000 and 5000 mg/l in the effluent compared to the recommended permissible limit of 2 mg/l.

1.4. Chemical behaviour of chromium in the soil

The interaction between the liquid and solid phase in soil is of most concern. Figure 1.3 shows the soil system model, which provides a convenient reference frame for the terrestrial transport and fate of chromium compounds (Katz and Salem, 1995). Movement of heavy metals within the soil will be in the solution phase, hence the chemical factors that control the distribution of metals between solid and solution phase, and the chemical forms in each phase, will influence the mobility of the metals. In brief, soil chemical reactions controlling mobility of heavy metals are broadly, adsorption/desorption or solubility/precipitation. In the first case the process is determined by the kind of surface phases present (see below) and the ionic species in solution. Solubility/precipitation is controlled by the concentrations and speciation of the ions in solution (Katz and Salem, 1995). Chromium solubility has been discussed in more detail on Section (1.1) for different chromium species at different pH.

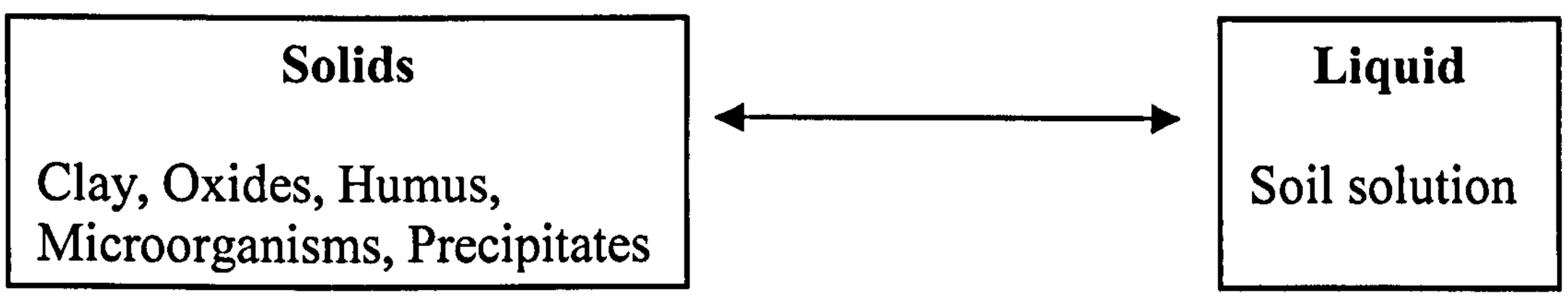


Figure 1-3 Model of the soil system.

1.4.1 Soil phase surfaces

Aluminosilicate clays have a permanent negative charge on the faces due to isomorphous substitution within the clay lattice. This charge is negative because it arises from the isomorphous substitution of elements of smaller positive charge for those of higher charge in the crystal lattice. The common substitution is of Si^{4+} in tetrahedral sheet by Al^{3+}, or Al^{3+} in octahedral sheet by another element such as Mg^{2+}, resulting in a net negative charge on the mineral . At the edge of the clay crystal, a pH dependent variable charge exists due to unsatisfied valences of broken bonds. This charge is analogous to that on the hydrous oxide (see below).

Humified organic matter is the dark, amorphous organic material found in soils formed by microbial breakdown of dead plant tissues and the synthesis of humified organic matter from the degradation products. The presence of certain functional groups on the humic polymer gives rise to both positive and negative charges. Charge development on organic matter is extensive and is entirely pH dependent. The important functional groups are:

Carboxyl (-COOH)

$$\text{-COOH} \rightleftharpoons \text{-COO}^- + \text{H}^+ \qquad \text{pk 3-5} \qquad \text{Equation 1-4}$$

Phenolate ($-C_6H_4OH$)

$$\text{-C}_6\text{H}_4\text{OH} \rightleftharpoons \text{-C}_6\text{H}_4\text{O}^- + \text{H}^+ \qquad \text{pk 7-8} \qquad \text{Equation 1-5}$$

The pk values show that in the environment the charge is always negative and the magnitude of the charge increases with increasing pH. Amino $-NH_2$ or sulfhydryl -SH groups could be a possible source of positive charge in many soils but they are less important.

Hydrous oxides, especially of oxides, hydroxides and oxyhydroxides of Fe, Al and Mn, also develop pH dependent charges which can be positive or negative charge. At one specific pH value there is a point of net zero charge (Figure 1.4). The zero points charge of the hydrous oxides most important in soil are as follows: MnO_2 approximately 4, Fe_2O_3, between 6.5 and 8, Al_2O_3 between 7.5 and 9 (Parks, 1965).

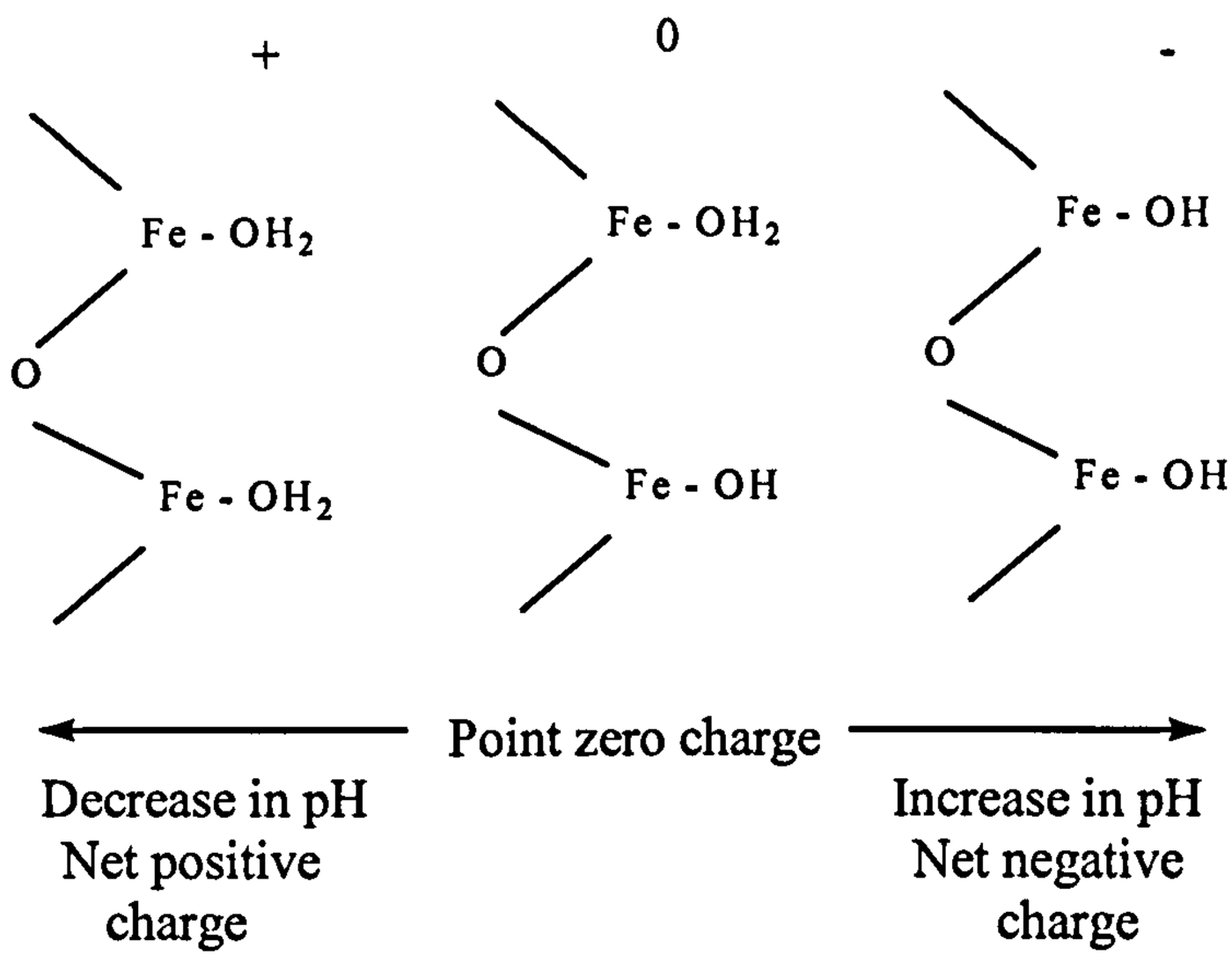


Figure 1-4 Representation the pH-dependent charges and the balance at point of zero charge.

The pH-dependent charge of soil particles varies with the pH at which the charge is measured. The positive charge is developed at pH below the point of zero charge and the excess negative charge developed at pH above the pzc. The source of pH dependent charge is considered to be the gain or loss of H^+ from the groups on the surfaces of soil solids with broken bonds which have unsatisfied valences.

Most temperate soils have a net negative charge because of the negative charges on the layer silicates and organic mater therefore the predominant ion exchange will be cation exchange. There is the possibility of anion exchange on amino $-NH_2$ and sulfhydryl –SH groups of soil organic matter and on positive charges on hydrous oxides and clay edges at pH below point of zero charge (Greenland and Hayes, 1978).

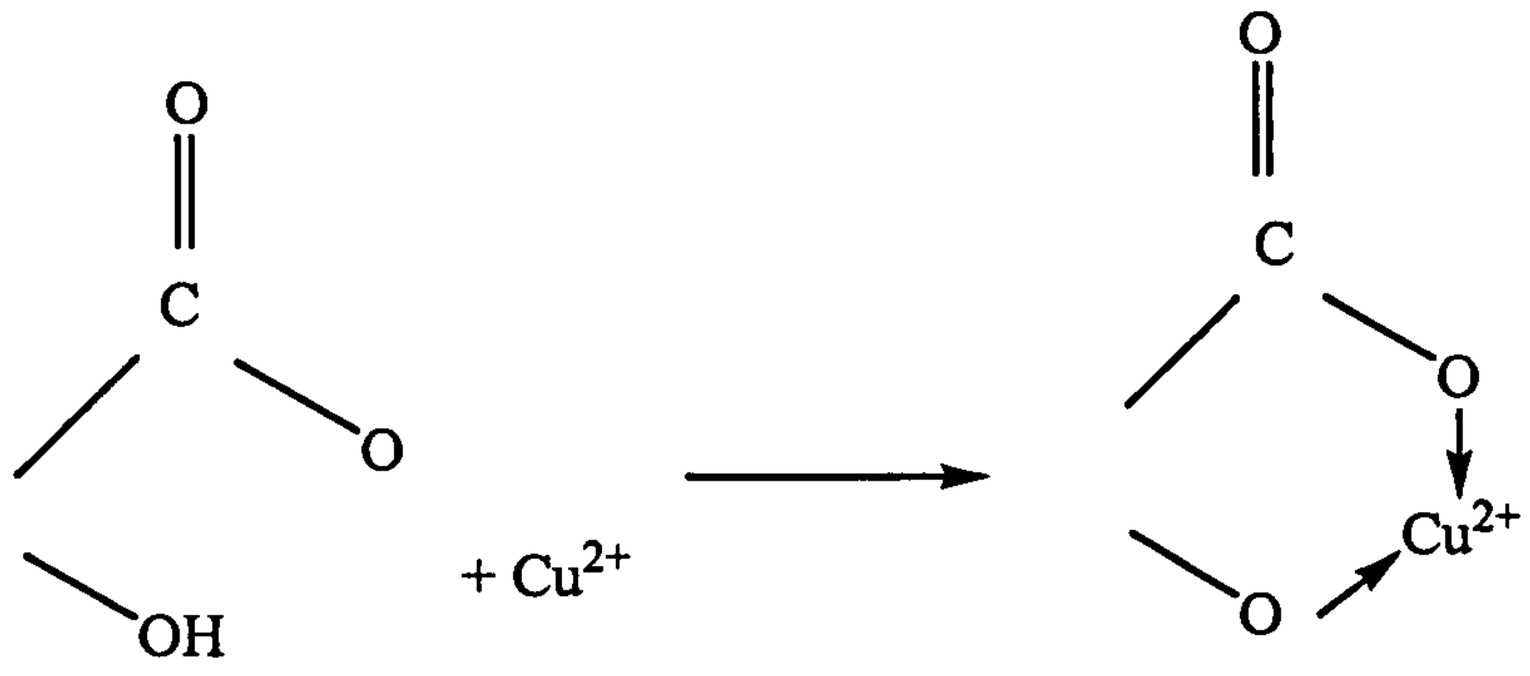
Ion exchange in soil involves the replacement of one adsorbed, readily exchangeable ion by another ion of the same charge in solution in contact with the surface. Cation exchange is the major reaction in the environment: Equation 1-6 shows Ca^{2+} in solution replaces K^{+} on a clay surface (X) as an example. Anion exchange can occur, but is of minor importance in the natural environment. The most important solid phase surfaces on which cation exchange occurs are silicate clays, humified organic matter and hydrous oxides (Talibudeen, 1981).

$$\underset{\text{Ions on solid Phase}}{2KX} + \underset{\text{Ions in solution}}{Ca^{2+}} \quad \underset{\text{Ions on solid phase}}{CaX_2} + \underset{\text{Ions in solution}}{2K^{+}} \qquad \textbf{Equation 1-6}$$

Chemisorption occurs when ions or molecules bind to the solid phase surface by covalent bonds, hydrogen bonds or Van der Waals forces. The main solid phase surfaces on to which anions and metals can be adsorbed are oxides and hydroxides of Fe, Al and Mn. These surfaces have a variable charge, which depends on pH as described above. Adsorption will be discussed later on (Section 1.8.3).

Complexation is the process whereby organic matter can react with metal cations to form organo- metallic complexes (Equation 1-7). The complex is particularly stable if more than one bond is formed (–chelation), as an example Cu^{2+} reacts with the function groups of organic mater Equation 1-8.

$$M^{+} + \text{-}LHy \quad \text{-}LM^{(x-y)+} + yH^{+} \qquad \textbf{Equation 1-7}$$



Equation 1-8

Metals complexed by high molecular weight organic compounds are immobilised, whereas low molecular weight complexes may retain the metal in solution at pH values higher than would be expected based solely on solubility considerations.

1.4.2. Chromium (III)

The main mechanism controlling the behaviour of Cr (III) in soil is solubility /precipitation (see Section 1.1). As shown in Figure 1-1, Cr (III) is insoluble above a pH of approximately 4, which is typical of most of the natural environment, and certainly true of chromium ore processing residue, which has a pH in the range 8-10. In acid environments of pH< 4, Cr (III) exists as the Cr^{3+} cation, which can be held on the negatively charged sites on the surface of soil components discussed in Section 1.4.1. (Puls et al., 1994). It is possible that Cr (III) could be mobile at pH > 4 due to the formation of complexes with humified organic matter, which have a greater solubility under these conditions than the uncomplexed Cr^{3+} ion (Nieboer and Nriagu 1988). Overall, however Cr (III) is relatively immobile and non-bioavailable in soil.

1.4.3. Chromium (VI)

Cr (VI) exists as anion; it is more readily extracted from soil and sediment particles and is considered the more toxic form. Chromium (VI) is typically in pH-dependent equilibrium in various forms, such as $HCrO_4$ and dichromate ($Cr_2O_7^{2-}$), with (CrO_4^{2-}) the predominant form at pH > 6 (McGrath, 1995).

The dominant factor controlling the behaviour of the Cr (VI) anion is the adsorption on to the oxide surfaces (Khaodhiar, et al. 2000). In the anionic stable form, $HCrO_4^-$ and CrO_4^{2-}, Cr (VI) could be attracted to positively charged sites on the surfaces of soil components, but this is a relatively unimportant process (Rai et al., 1989). The hydrous oxides commonly coat other soil materials and chemisorption of Cr (VI) on to these surfaces, occurs over a wide range of pH regardless of surface charge. Weak acid anions have maximum adsorption at pH values about equal to their p*K* values (Bohn et al., 1985). Adsorption of Cr (VI) characteristically decreases with increasing pH, with the greatest adsorption occurring as pH decreases below 6 which is approximately p*K* of CrO_4^{2-} (Puls et al., 1994).). The adsorption envelope for chromate adsorption on to iron -oxide -coated sand shows that the chromium adsorption decreased with pH and an inflexion point at approximately pH 6 (Greenland and Hayes, 1981). Little or no adsorption occurs above a pH of 8.5 (Khaodhiar et al., 2000).

The competing effect due to the presence of strongly adsorbing anions, such as AsO_4^{3-}, SO_4^{2-} and PO_4^{3-} decreases chromate adsorption due to electrostatic effects and direct competition for adsorption sites. The presence of metal ion such as Cu^{2+}, Cd^{2+} and Pb^{2+} enhances chromate adsorption on iron (III) hydroxide, probably due to the increase in adsorption sites as a result of coprecipitation of metal ion with iron (III) hydroxide (Khaodhiar, et al. 2000). Above a pH of 8.5, Cr (VI) would be entirely unretarded (Nieboer

and Nriagu 1988). Concerns for public health arise from the greater mobility of hexavalent chromium, coupled with its greater toxicity and the alkalinity of contaminated sites (Katz and Salem, 1995).

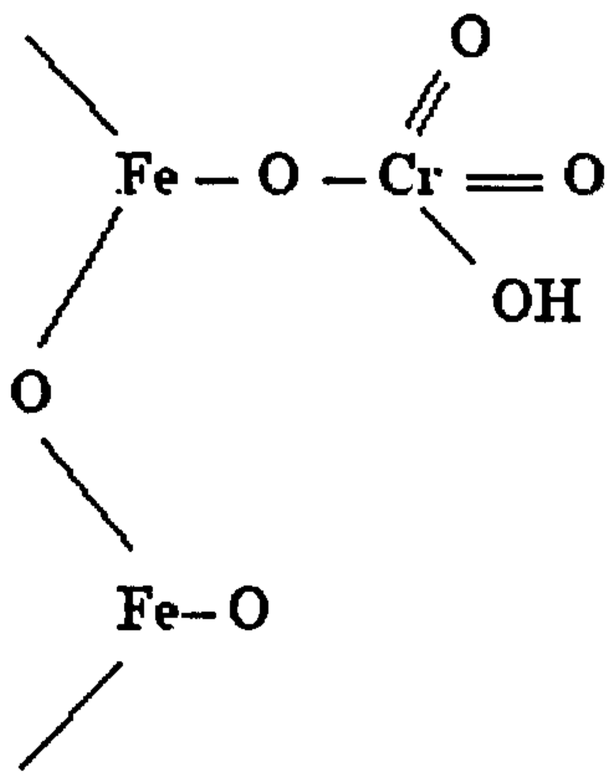


Figure 1-5 Chromate adsorbed at an iron oxide surface

Chromium (VI) is the stable form in equilibrium with atmospheric oxygen. However, Cr (VI) is a powerful oxidising agent and will readily react with soil organic matter to form Cr (III) (McGrath, 1995). Soil pH and the presence of iron oxides, soil organic matter and low soil oxygen levels influence reduction (Environmental Canada and Health Canada, 1994). Certain elements and compounds enhance the mobility of Cr. As an example, Mn (III, IV) oxides could oxidise Cr (III) to Cr (VI) at pH 5 because the range of pe values for reduction of Mn (12.8 - 16.7) is greater than that for Cr (VI) reduction (10.9) (Sparks, 1995). This is particularly important in the case of waste disposal sites where Fe, Mn-rich sediments, Fe-containing groundwater or wastes from the metal and leather industry can be found in the system.

1.5. Chromium contamination issues in Glasgow

One of the largest producers of chrome in the world from 1810 to 1968 was at Shawfield in South-East Glasgow Scotland. It was operated by J.J. Whites chemical works and chromite ore processing residues from the work were used as infill material (Farmer et al., 1999). The Shawfield works was eventually closed after trading for 148 years. Glasgow City Council indicated 15 sites where high concentrations of hexavelant chromium penetrated 10 m in places, the maximum concentration 65000 mg/kg and the mean was 4000 mg/kg of total Cr. The maximum Cr (VI) concentration was 16000 mg/kg and the mean 700 mg/kg at 15 sites in Glasgow (Bewley et al., 2001).

The manufacture of oxide chromium started in 1919 at Whites factory. In 1945 the process was changed to bichromate crystallising. Therefore, the types of waste product changed from chrome ore dust to liquor and then to residue deposits. Large amounts of heavy metals, chromium (III) and (VI), acids, cyanide, arsenic and benzene were all dumped as waste products due to the chromium ore refining process.

The dust levels increased in surrounding streets as a result of fires and many explosions, these were recorded as complaints by local residents. 25 years after the factory closed, the extent of illegal toxic dumping was discovered during development the areas. It was widespread throughout areas of Cambuslang, Carmyle, Rutherglen, Toryglen and Eastfield. In 1991 the first report from The Glasgow Environmental Health Department gave information on the illegal sites, through former employees, who had driven the waste to various dumps. Nine contaminated sites were confirmed, which contained total chromium levels between 4,380 mg/kg and 26,150 mg/kg.

In 1992 one program on television exposed the high incidence of child leukemia in the Cambuslang and Rutherglen areas. Some members of public, actively campaigning against toxic waste, formed c.c.r.a.p.(Cambuslang, Carmyle and Rutherglen against pollution). They hold open days as well as giving support to individuals and families affected by both the working conditions at factory and the subsequent effects of the dumped waste.

The Environmental Health Report issued in 1992 advised that there was no apparent threat to human health other than in situations of direct human contact (Levy et al., 2001). They advised, for example, that children should not be allowed to play on or near contaminated land. It stated that football pitches in grassy areas would be replaced and not be reused. Most of the contaminated sites were found to be children's play areas where the fencing and "Keep Out" sign remain largely ignored. Only two areas have had remedial work carried out by the application of heavy-duty plastic covering, rubble and topsoil and some areas were treated with sewage sludge to improve the vegetation cover, but still concerns remain about the poor growth on some areas. Many factories, including food related factories, are built on the land where the chemical works once stood; also Rutherglen Maternity Hospital is built on a toxic waste dump. Today, there are many major developments underway on known toxic waste dumps.

In 1993 Dames and Moore on behalf of Glasgow City Council investigated of remedial options for the Glasgow sites. The key objectives of investigation for each treatment technique were to achieve (1) maximal reduction of Cr (VI) present in soil and/or groundwater such that it did not pose a risk to potential receptors and (2) maximal reduction in the overall leachability of Cr (VI) such that it no longer posed a risk to controlled water.

1.6. Soil Guideline Values for Chromium according to land-use

Risk assessment relies on investigating the likely presence and significance of a pollutant linkage between a **source** of contamination and **receptor** by a **pathway** (Figure 1.6). This underlies Part IIA of the (Environmental Protection Act, 1990), which is the legislation dealing with contaminated land. This will in general involve a risk assessment to consider a threshold above which harm may be caused based on an interpretation of the conceptual model (DETR Circular 2/2000, 2000).

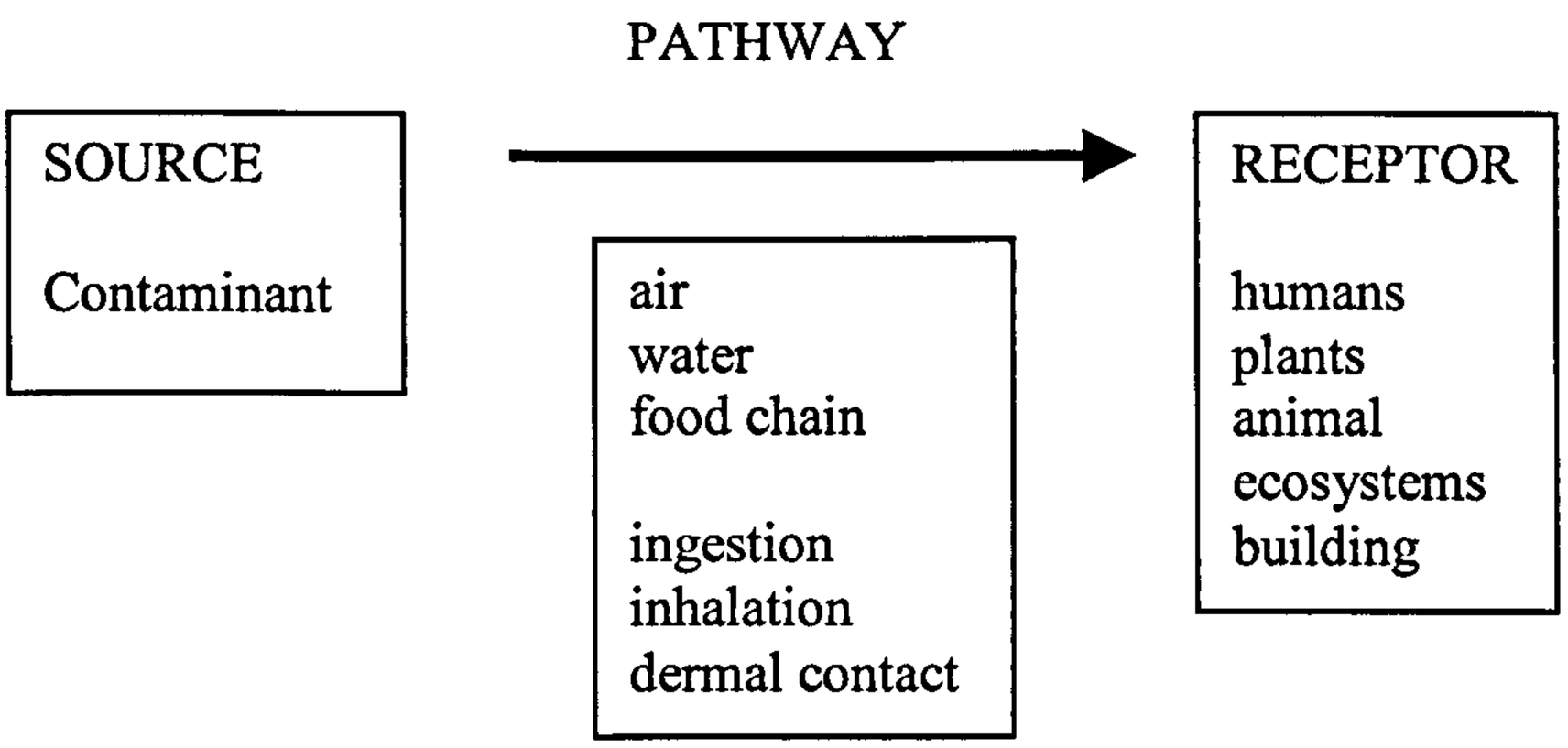


Figure 1-6 Pollutant Linkage Model

The pollution linkage model can be applied to COPR and Cr contaminated soil, taking into account the chemical behaviour of Cr in soil described above. For Cr (III), which is relatively immobile, the major pathway for transmission to humans will be inhalation or ingestion due to dust blow, or ingestion following dermal contact. Thus those at most risk will be people living in close proximity to unvegetated COPR dump sites, who could be exposed to dust over a long period, and people who come in to contact with the waste material. Children are a particularly important group in this latter category, as they may

play on the dump sites, (there was evidence of this at the study sites used in this project), and are at risk of ingestion of Cr following handling of the waste. The WEL for Cr (III) is high (see Section 1.2.) and so overall risk to human is relatively low. Because of its poor solubility, and hence mobility and bioavailabilty, there is little risk to plants or ecosystems (especially water) from Cr (III).

The risks due to Cr (VI) are much greater due to its toxicity and carcinogenicity, and hence its low WEL value. Thus if Cr (VI) is present in the waste or contaminated soil, the risks to humans due to dust blow and physical contact described above are much greater than for Cr (III). There is a known history of high incidence of cancer of the respiratory tract in workers handling chromium compounds. Thus the presence of Cr (VI) would pose a much greater risk to local residents exposed to dust blow over a prolonged period and to children playing on contaminated sites. Because of its greater mobility, Cr (VI) poses a greater threat to plants and ecosystems as it can be transported in solution to groundwater and surface waters.

Soil Guideline Values are a screening tool for use in the assessment of land affected by contamination. They can be used to assess the risks posed to human health from exposure to soil contamination in relation to land-use (DEFRA, 2002d). They represent "intervention values", indicators to an assessor that soil concentrations above this level might present an unacceptable risk to the health of site-users and that further investigation and/or remediation is required.

Soil Guideline Values have been developed on the basis of many critical assumptions about possible exposure to soil contamination and the development of conceptual exposure models to describe different land-uses. So it is important that a risk assessor uses soil

guideline as a component of an overall risk assessment and management strategy for a site in accordance with good practice (DEFRA, 2002b).

The Soil Guideline Values for chromium contamination are summarised in table below. The Soils Guideline Values have been estimated using the Contaminated Land Exposure Assessment (CLEA) model and it is assumed that all chromium present in the soil is chromium (VI).

Standard land-use	Soil Guideline Value (mg/ kg dry weight soil)
Residential with plant uptake	130
Residential without plant uptake	200
Allotments	130
Commercial/industrial	5000

Table 1-3 Soil Guideline Values for chromium as a function of land-use

Notes

1. **Based on total chromium concentration in the soil.**
2. **Based on intake of chromium only and compared with oral tolerable daily soil intake (TDSI) value.**
3. **Based on sandy soil as defined in CLR10** (DEFRA, 2002d)

It is difficult to do comparison between different guideline values and transpose technical guidance from one authority to another (DEFRA, 2002c). The Interdepartmental Committee for the Redevelopment of Contaminated land (ICRCL), which was the guideline system used in the UK prior to CLEA, published trigger concentration for total and hexavalent chromium (ICRCL, 1987). The threshold concentration for total chromium for domestic gardens and allotments was 600 mg/kg and that for park, playing fields and open space was 1000 mg/kg. The threshold concentration for hexavalent chromium for domestic gardens and allotment was 25 mg/kg. There is little information available about the method used in these values, the hexavalent chromium extracted by 0.1 M HCl adjusted pH 1 at 37^0C.

Guide values and quality standards used in Netherlands for assessing soil contamination give a reference value of Cr concentration 100 mg/kg in natural land contaminated only

from atmospheric deposition, and the intervention value for all land-uses is 380 mg/kg, where the soil must be cleaned-up (Alloway, 1995). Therefore direct comparison with the new Soil Guideline Values is not easy.

1.7. Assessment of Chromium release from soil:

When the main problems of trace metals in the soil were deficiencies, it was usually sufficient to know how much of an essential trace was available to an extractant, such as dilute acetic acid, distilled water, ethylene diamine tetracetic acid (EDTA), diethylene triamine pentacetic acid (DTPA) (Beckett, 1989).

These problems have led many workers to employ specific extractants to identify the forms of combination of trace metals in sludge or soil, or in geological sediments. For example, chromium waste has been assessed by aqua regia digestion and extraction with acetic acid, KH_2PO_4 and leaching with deionised water (Facchinelli et al., 2001). Measures of total soil Cr [the sum of Cr (III) and Cr (VI)] is accurately quantified by acid digestion of the soil that includes the use of HF to dissolve silica-bearing minerals that may occlude insoluble forms of Cr (James, 2001)

However, in order to design pragmatic remediation treatments and risk assessment with scientific understanding, an experimental approach based on conventional chemical analysis should be integrated with mineralogical analysis (Thomas et al., 2001). Farmer et al. (1999) used X-ray powder diffractometry (XRPD) and scanning electron microscopy (SEM) combined with energy dispersive X-ray microanalysis (EDX) to identify and quantified solid and solution phases species of chromium. Thomas et al. (2001) found that solid-phase species of chromium characterisation has demonstrated the presence of mineral components, and that some of these components might contain Cr (VI). In the solution-

phase, Cr (VI) has been found to be the most abundant species, but the presence of Cr (III) in solution possibly as organically bound species.

The single and sequential extraction schemes were critically examined in relation to the speciation of the heavy metal in soil (Ure et al., 1993). Davidson et al., (1994) found the sequential extraction procedure is sufficiently repeatable and reproducible for application in speciation studies. The amount of metal removed by the procedure correlated well with those removed by pseudo-total acid digestion of the sediment used.

The measurement of total chromium using atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) dose not depend on the species of chromium, fortunately the colorimetric method to determine soluble Cr (VI), based on its reaction with 1,5-diphenylcarbazide, is accurate and precise for quantifying soluble Cr (VI) in soil extracts (Bartlett and James, 1979; Bartlett and James, 1996).

Because of the difference in risk and toxicity between soluble and insoluble forms of Cr it is important to be able to distinguish between them analytically. As described in section (1.4), Cr (III) is generally insoluble under environmental conditions, although some soluble organic complexes may occur (Vitale et al, 1997b). Thus for Cr (III) the risk is primarily due to wind blown dust, and so a total value is usually sufficient. For Cr (VI), which is more toxic and soluble, the quantification of soluble, exchangeable (chemisorbed) and insoluble forms of Cr (VI), summed to equal total Cr (VI) in soil and waste materials, has direct application to assess the human health risks and environmental hazard from potential Cr (VI) exposure (James et al., 1995; Vitale, et al., 1997b; Morales-Munoz et al., 2004; Pettine and Capri, 2005). The risk from Cr (VI) in wind blown dust requires a measure of total Cr (VI), but the soluble and exchangeable fractions of Cr (VI) are useful parameters for estimating soil levels of Cr (VI) that may leach to groundwater or surface water.

The most common standard method is EPA method 3060A, which is a hotplate extraction using 0.28 M Na_2CO_3/0.5 M NaOH and is prescribed for the dissolution of both water-soluble and insoluble forms of Cr (VI) (James et al., 1995; Vitale et al., 1997a). This has been exhaustively tested for removal of insoluble chromates, such as lead and barium chromate. James et al. (1995) reported almost complete recovery of a $PbCrO_4$ spike (91-96%), but a poor recovery of a $BaCrO_4$ spike (63-78%).

In many cases, however, a measure of Cr (VI) that can readily leach from a soil or waste is what is required and a number of extractants have been used including deionised water, buffers and dilute salt solutions (Table 1.4). The water and salt solution extractants were used to mimic the leaching of soil or waste by rainwater, whereas the buffers contain an anion such as phosphate or carbonate that will exchange with chemisorbed chromate. In this project the leachable Cr (VI) was determined by using water extract. (Bartlett and James, 1996) proposed that readily soluble Cr (VI) was determined after soil extraction with deionised water. Panichev et al. (2003) reported a protocol for determining Cr (VI) which can be naturally leached from soil by using deionised water and bubbling CO_2 through the suspension to mimic the dissolution of atmospheric CO_2. There was a good correlation between the concentration of dissolved CO_2 and the amount of Cr (VI) leached. Cr (VI) was leached from the soil at all concentrations of CO_3^{2} ions, even that arising from dissolved CO_2 at normal atmospheric pressure. The presence of soluble Cr (III) in samples can be assessed by a water extraction and analysing the resultant leachate for both Cr (VI) and total Cr. Soluble Cr (III) is determined by subtracting the results of the Cr (VI) from the total chromium values (Vitale et al., 1997b).

The reported analytical techniques for the quantitative measurement of Cr (VI) in aqueous solution and for the measurement of total Cr in the solid phases are summarised in Table (1.4).

Table 1-4 Summary of literature methods for Cr (VI) determination in solids

Reference	Extractant used
Total Cr (VI)	
(EPA (3060A/7196), 1996)	Carbonate-hydroxide extractant (0.28 M Na_2CO_3 /0.5 M NaOH; pH 11.8), $MgCl_2$ and 1M phosphate buffer at 90 – 95° C. The Mg^{2+} ions prevent the oxidation of Cr (III).
(United States Occupational Safety & Health Administration(OSHA), 1998.)	10% Na_2CO_3/2%$NaHCO_3$ in the presence of phosphate and magnesium
Soluble and exchangeable Cr (VI)	
(Rudel and Terytze, 1999)	Phosphate buffer (pH 8) + 0.37 M $Al_2(SO_4)_3$, plus 1 ml of 0.93M Na_2SO_3 to reduce oxidising compounds other than Cr (VI).
(James et al., 1995)	Phosphate buffer (5mM K_2HPO_4/5mMKH_2PO_4, pH 7).
(DIN 19730, 1997.)	1 M NH_4NO_3
(Geelhoed et al., 2003)	1mM NaCl
(James et al., 1995)	Deionised water
(Panichev et al., 2003)	Deionised water with bubbling CO_2

An ideal extraction method would extract Cr efficiently without converting metal ions from one oxidation state to another (inter-conversions of Cr (VI)-Cr (III)). Any redox changes occurring in the extraction should therefore be of concern. Vitale et al. (1997b) compared the effectiveness of the alkaline extraction method (Method 3060A) in contrast with four others to solubilise sparingly soluble $PbCrO_4$ spiked into four diverse soil materials (quartz sand, chromite ore processing residue-enriched soil, anoxic sediment and a loamy- textured soil. They observed that the heated alkaline method extracted about 90% of the $PbCrO_4$ spike from three of the materials used, but that $PbCrO_4$ was not recovered from the anoxic sediment, which is a highly reduced system and so Cr (VI) would be converted to Cr (III). Distilled water and phosphate buffer extractions were also used to quantify and operationally define soluble and exchangeable forms of Cr (VI). No Cr (VI) spike was extracted from any of these soils by distilled water and phosphate buffer. In the quartz sand and loamy sand, this is due to Cr (VI) not being solubilised. In the anoxic sediment, it may be that Cr (VI) was solubilised and then reduced to Cr (III) by sulphides present (Vitale et al. 1997b).

A similar analytical problem has been encountered when assessments are made of Cr exposure in the workplace. Ashley et al. (2003) investigated different analytical methods to determine Cr (VI) in workplace atmospheric samples and related this to chromium speciation (water soluble- insoluble forms) to provide a means for occupational exposure assessment. They discussed the advantages and disadvantages of methods for determination of soluble Cr (VI) that use either deionised water or ammonium sulphate-ammonium hydroxide buffer solution as extractant. The ammonium sulphate-ammonium hydroxide buffer solution dissolved sparingly soluble Cr (VI) species, but water was considered better if it is desired to measure only soluble Cr (VI). Extraction with water

could yield low results for soluble Cr (VI) if the samples contain substances that can reduce Cr (VI), for example Fe in welding metal dusts (Ashley et al., 2003).

1.8. Treatment technologies for contaminated soil samples

Clean-up standards for Cr-contaminated sites require remediation strategies that will protect human health, ecosystem function, and groundwater quality in the urban areas. The minimization of the environmental impact of heavy metals in aquatic systems and leachates requires the application of different remediation strategies such as: oxidation/reduction reaction, precipitation, ion exchange, adsorption-desorption, electrochemical, membrane filtration photoremediation, and bioremediation. I have chosen in this thesis to focus on the oxidation/reduction reaction as one of the traditional remediation and also study the adsorption-desorption on a solid phase one of development clean-up strategy.

1.8.1. Oxidation - Reduction reaction

The toxicity of chromium depends on its oxidation state as explained previously in Section (1.1). Because Cr (III) is essentially non-toxic, traditionally the reduction of Cr (VI) to Cr (III) has been considered a clean-up strategy without changing the total Cr content of a soil. Acceptable remediation of Cr (VI) contaminated soils by reduction depends on three principles: the reduction of insoluble and soluble forms of Cr (VI) to forms of Cr (III) that are inert to reoxidation, the absence of unwanted reaction products due to the oxidation of the reducing agent, and the prevention of marked changes in soil pH and Eh (James et al., 1997). There are a number of reducing agents that have been applied successfully for the treatment of chromium-contaminated wastes/groundwater. Reductants include ferrous

compounds, reduced sulphur compounds, zero valent iron, and hydrazine. Sodium hydrosulphite (dithionite) can be used in alkaline conditions, but is not usually cost effective (McLeod, 2001).

Developing such remediation by reduction strategies is a complex and controversial issue because Cr (III) can oxidise to Cr (VI), and the rate and extent of Cr (VI) reduction is strongly dependent on soil condition (James, 1996).

Where soils have high Cr, one key issue that complicates these efforts is the possibility that Cr (III)-to-Cr (VI) oxidation by manganese (III, IV) (hydr) oxides occurs in soil (Bartlett and James, 1979; Bartlett and James, 1996). Regulatory agencies have sometimes assumed that all forms of Cr (III) will oxidize to Cr (VI); while at other times, they have assumed that none of it will do so. Because of this situation, reliable mechanisms are needed to assess the possible extent of oxidation of diverse forms of waste and soil-borne Cr (III), how effective remediation-by-reduction strategies are, and how soil redox status can predict the valence state stability of Cr.

Chemical and electrochemical treatment processes have been used to treat hexavalent chromium in waste and effluent streams, traditionally involving the reduction of hexavalent chromium to a trivalent form (typically in acidic media). It is necessary to adjust the pH to the optimum for precipitation of trivalent chromium as the hydroxide (ideally pH 9) (McLeod, 2001).

James, (2001) considered that thermodynamically possible reduction reactions of Cr (VI) by Fe (0), Fe (II), hydroquinone, and bisulphide convert the anionic, soluble, and toxic form of Cr in soils to cationic, less soluble Cr (III), and changes in pH and Eh (pe) of soils must also be considered.

Terry, (2004) demonstrated that water which has high chromium concentration could be purified to a level that was not statistically different than the EPA limit of 0.1 mg/l, using ion exchange on hydrotalcite Zhao, et al., (1998) reports the performance of a new type of anion exchange, referred to as polymeric ligand exchange or PLE pertaining to chromate removal. The exchanger can very selectively remove trace concentration of chromium from the background of competing sulphate, chloride, bicarbonate, and nitrate anions.

1.8.2. Phytoremediation and bioremediation

Phytoremediation and bioremediation is an attractive alternative to conventional clean-up method because it is comparatively inexpensive and environmentally friendly.

Phytoremediation is defined as the use of green plants to remove pollutants from the environment or to render them harmless. Pulford and Watson examined the tolerance and potential use of trees such as birch and willow for phytoremediation of chromium-contaminated sites (Pulford et al., 2001; Watson et al., 1999). This study confirmed that chromium was poorly taken up into the aerial tissue but held predominantly in root, so the prospects for using trees as phytoremediators on chromium-contaminated sites are poor. Chromium accumulation in fodder radish treated with chloride, picolinic acid, and separately added chromium chloride + picolinic acid and with chromium picolinate has found this phenomenon could useful in phytoremediation of chromium contaminated soils (Simon et al., 2001). Duckweeds are commonly used plants in phytoremediation, and Dirilgen and Dogan, (2002) revealed that the oxidation state of chromium as well as its concentration in media controlled the growth and the metal accumulation in duckweeds (*Lemna minor*).

Zayed and Terry (2003) investigated chromium in the environment and the factors affecting biological remediation and having the chromium concentration in a variety of plants growing on uncontaminated or Cr-rich soil. More than 99 % of the absorbed Cr remained in the root where it is reduced to Cr (III) species in a short time. Therefore the food chain is well protected against Cr toxicity.

Bioremediation uses bacteria and fungi to eliminate attenuate or transform contaminating substances and to convert contaminants to harmless or more environmentally acceptable products. (Evans et al., 1997) for the first time reports on Cr (VI) reduction through biological mechanisms in a continuous-flow, biofilm reactor without the need to constantly resupply fresh Cr (VI)-reduction cells. Studies by (Smith, 2001) have shown that it might be possible to use sulphate-reducing bacterial biofilms in a bioreactor configuration to treat chromium-contaminated wastes prior to discharge into the environment. Bielefeldt and Tseng, (2002) demonstrated that indigenous microbes are suitable for in situ Cr (VI) treatment, regardless of redox or electron acceptor availability, provided that sufficient carbon is available

1.8.3. Adsorption

Adsorption is critical in many geochemical processes such as the removal of contaminants from ground and surface water in many of chemical processes (Garcia-Sanchez et al., 1999). The section below discusses the definitions of sorption and mechanisms.

1.8.3.1. Definition of sorption and mechanisms

Adsorption is the net accumulation of matter at the interface between a solid phase and an aqueous solution phase. Adsorbate is a dissolved species, or multiple species, that becomes concentrated at the surface of some solid, which is the adsorbant (Jenne, 1998). Adsorptive is a molecule or an ion in the soil solution that potentially can be adsorbed.(Sposito, 1989)

Over 100 years there have been differences in opinion over the definition of adsorption. In 1918, Langmuir defined adsorption as a "chemical process with similarities to the chemical bonding between atoms in a crystal with unsatisfied bond in contact with solvent water". Also, adsorption defined by the Soil Science Society of America (1996) as "the process by which atoms, molecules, or ions are taken up from the aqueous phase and retained on the surfaces of solids by chemical binding" (Jenne, 1998)

Definition of the mechanisms of adsorption in the literature can be confusing at times due to differences accorded by various researchers. There have been different definitions of the mechanism of adsorption, especially under the terms complexation and chemisorption. Sorption processes can be categorized into either adsorption or precipitation processes.

Precipitation can be defined as an accumulation of a substance to form a new bulk solid phase. Precipitation and adsorption concepts imply a loss of material an aqueous phase, adsorption is inherently two-dimensional and precipitation is inherently three-dimensional (Sposito, 1984). Presumably adsorption, being two dimensional, is limited by the surface area of the adsorbant. The surface area is important for sorption but it is the availability of this area to metal ions that is more important.

The complex adsorption mechanisms on particle surfaces can take place via different mechanisms. The inner sphere surface complex shows the loss of one or more OH groups from the inner-coordination sphere of the metal ion for one or more ligand coordinating atoms on the surface of the particle in ligand – exchange reaction. Inner sphere complex mechanisms are likely to involve ionic as well as covalent bonding and this is defined as specific sorption. The outer sphere surface complex includes the cation solvation shell. The outer sphere surface complex mechanisms of adsorption involve almost exclusively electrostatic bonding and is termed non-specific due to the weak dependence on the electron configuration of the surface group and adsorbed ion (Sposito, 1989).

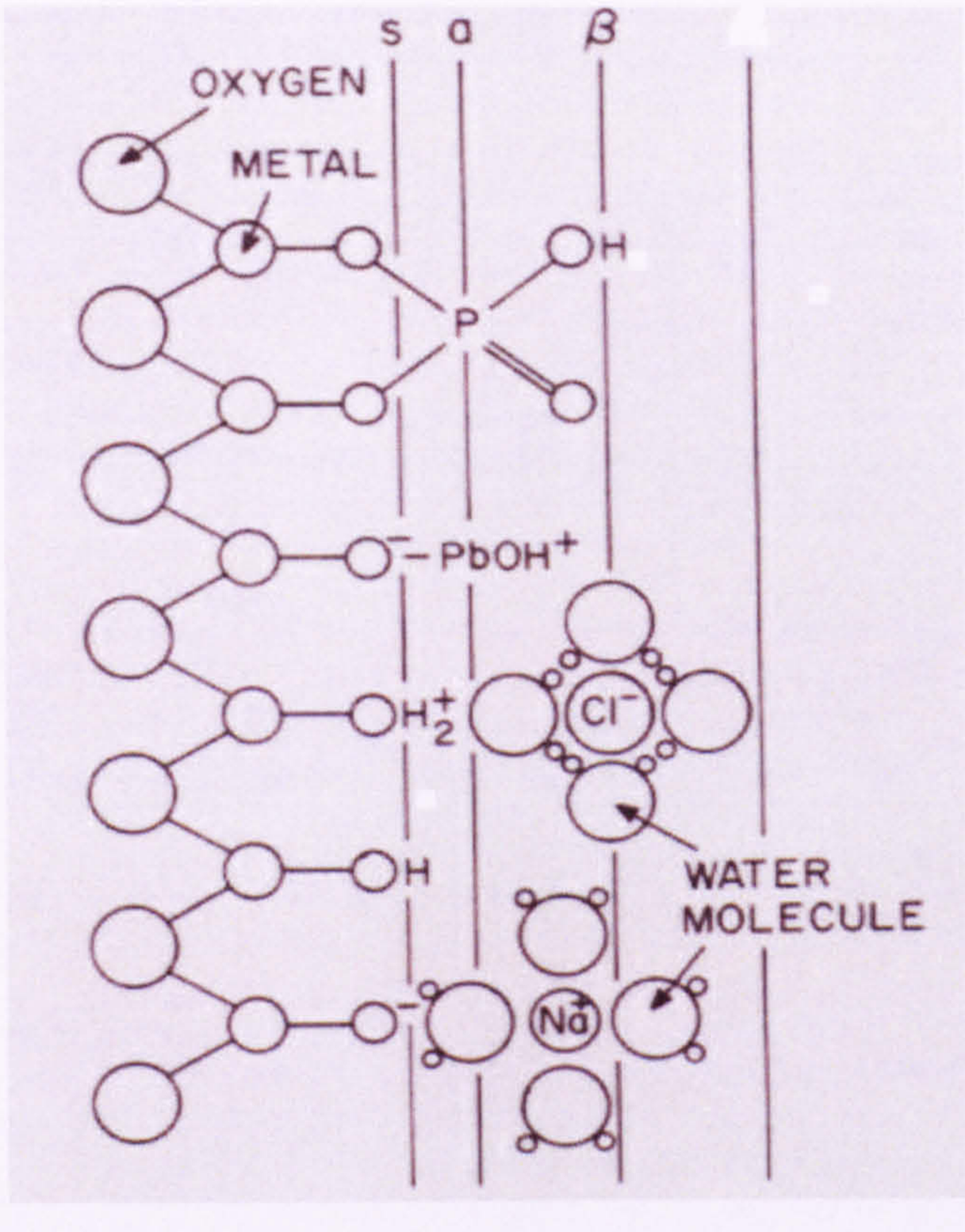


Figure 1-7 A schematic portrayal of an inorganic hydroxyl surface, ("s") showing planes associated with surface hydroxyl groups, ("a") inner-sphere complexes, ("β") outer-sphere complexes (Sposito, 1984).

1.8.3.2. Experimental determination of adsorption

Adsorption is studied experimentally by two main basic laboratory operations: (1) reaction of the sorbent with a solution of known composition for a prescribed period of time, (2) chemical analysis of the sorbent, solution, or both to determine their composition.

The reaction in step 1 can take place either with the solution mixed uniformly with the sorbent particles as a "batch process" or with the solution in uniform motion relative to a column of the sorbent as a "flow-through process" (Sposito, 1989).

The chemical analysis in step 2 of the batch process is carried out after isolation of the sorbent from the reaction solution by centrifuging or filtering. In flow-through process the composition of the effluent solution is analysed to determine the changes caused by adsorption.

The amount of metal ion adsorbed moles per kilogram at time t, X_t, of adsorbent is calculated with the Equation (1-9):

$$X_t = ((C_0 - C_t)\, V) / m \qquad \textbf{Equation 1-9}$$

t = equilibrium contact time

C_0 = initial solution metal concentration

C_t = solution metal concentration at time

V = volume of solution

m = mass of sorbent used

adsorption is determined experimentally by measuring how much of a solute a particular solid can sorbs. In the batch system the graph of amount sorbed (X) against equilibrium concentration (C) is called an adsorption isotherm. Adsorption isotherms are convenient

for representing the effects of adsorptive concentration the surface excess. In the literature there are different types of adsorption isotherm curve shows in Figure (1.3).

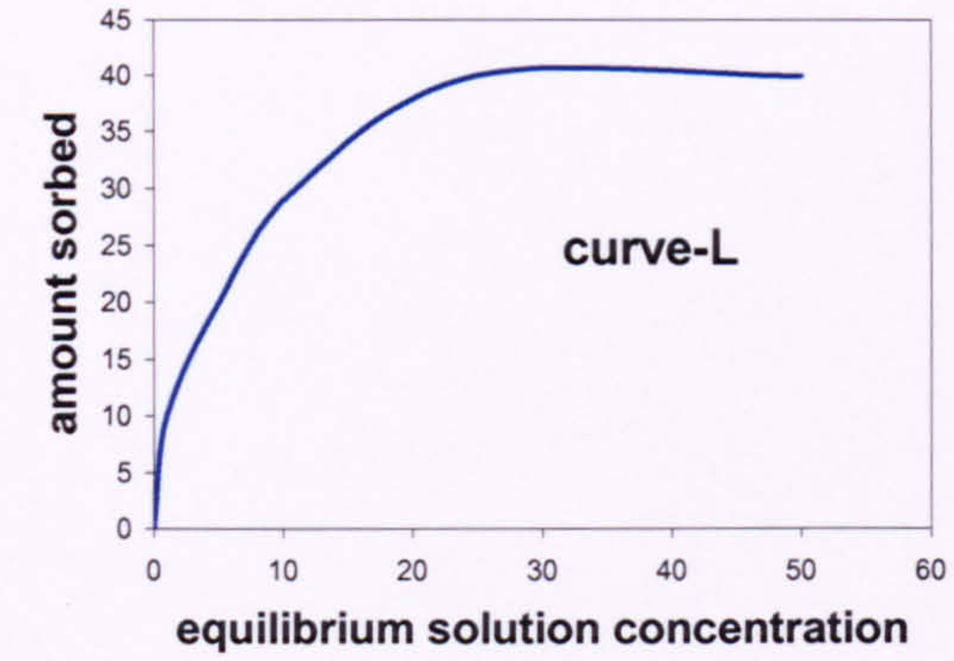


Figure 1-8 Typical adsorption isotherm curve L-shaped, S-shaped and H-shaped (Sposito, 1989)

The L-curve Figure (1.3) isotherm is the resultant effect of a high relative affinity of the sorbent particles for the adsorbate at low surface coverage with a decreasing amount of sorbing surface as the surface excess of the adsorbate increases.

An initially small slope that increases with adsorptive concentration characterizes the S-curve isotherm. This behaviour suggests that the affinity of the sorbent for the adsorbate is less than that of aqueous solution. The H-curve isotherm is an extreme version of the L-curve isotherm. The characteristic large initial slope (relative to the L-curve) suggests a very high affinity of the sorbent for an adsorbate. This condition is usually due to significant inner sphere complexation.

The adherence of experimental sorption data to an adsorption isotherm equation provides no evidence as to the mechanism of a sorption process in the solid phase, but two such equations are commonly used.

Langmuir equation

The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir equation predicts the maximum amount of metal that can be adsorbed. Langmuir isotherm constants were calculated from the following linearized for Equation (1-10):

$$C_e/X_e = 1/X_{max}b + C_e/X_{max} \qquad \textbf{Equation 1-10}$$

Where X_{max} and b are Langmuir constants determined from the slope, $1/X_{max}$, and intercept, $1/X_{max}b$, of the plot, indicative of maximum adsorption capacity (mg/g) of adsorbent and bonding energy of adsorption, respectively, C_e is the remaining concentration of adsorbate after equilibrium (mg/l) and X_e is the amount adsorbed at

equilibrium (mg/g) (Kadirvelu et al., 2001). The Langmuir constant is the reciprocal of the slope ($1/ X_{max}$) and the bonding constant b is given by slope/intercept.

Freundlich isotherm

Freundlich isotherm assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption and that the amount adsorbed increases infinitely with an increase in concentration. The Freundlich isotherm is expressed as Equation (1-11):

$$X_e = K_f \cdot C_e^{1/n} \qquad \textbf{Equation 1-11}$$

Where K_f and n are constants of Freundlich isotherm incorporating adsorption capacity (mg/g) and intensity, while C_e and X_e are the remaining concentration of adsorbate after equilibrium (mg/l) and the amount adsorbed at equilibrium (mg/g), respectively. Taking logarithm for the Eq (1-6), a linearized form of Freundlich isotherm can be represented as follows Equation (1-12).

$$\log X_e = \log K_f + 1/n \log C_e \qquad \textbf{Equation 1-12}$$

Linear plots of log X_e versus log C_e, allow K_f and n, to be calculated from the intercept and the slope of the plots (Kadirvelu et al., 2001). Where (0<n>1) those depend upon the nature of the adsorbant, and adsorbent, and the values of system variables.

Langmuir equation and Freundlich isotherms have been used to model the sorption of metals, (cationic and anionic), onto a wide variety of sorbent. Kadirvelu et al. (2001) used the Langmuir isotherm and Freundlich isotherm to investigate the feasibility of using carbonized coir pith for the removal of Ni from aqueous solution. Feng, et al. (2004) found the agricultural waste such as rice husk ash was suitable adsorbent for the adsorption of lead and mercury ions from aqueous water and the adsorption isotherms fits both the

Langmuir and Freundlich isotherms. However, in this work langmuir equation has been applied to measure the capacity of different sorbents to adsorb chromium from solution.

Adsorption of heavy metals such as Zn, Cu, As, Pb, Cd and Tl onto several clays, iron oxides and hydroxides and local unpolluted soils was examine by (Garcia-Sanchez et al., 1999). Iron-oxide-coated sand in single-solute and multi-solute systems was studied to adsorbed copper, chromium, arsenic (CCA) (Khaodhiar et al., 2000).

A lot of research has studied the adsorption of chromium from contaminted sites and water by different kinds of adsorbent materials, such as activated charcoal (Jayson et al., 1993), activated carbon (Aggarwal et al., 1999), coconut shell charcoal (Babel and Kurniawan, 2004). In 2002 Dakiky used low cost abundantly available adsorbents to adsorb chromium (VI) from industrial wastewater and showed that the adsorption process is satisfactory and selective for Cr (VI).

1.9. Aims

The aims of this thesis are to investigate the assessment of chromium contamination in soil and it is potential remediation.

1. To assess total chromium and hexavalent chromium in Glasgow soils at a known chromium dumpsite and more widely around Glasgow.

2. To consider clean-up strategies for chromium contaminated sites to remove Cr (VI) or reduce it to Cr (III), which is less toxic. From that this project will investigate the oxidation- reduction reactions of Cr (VI) and Cr (III) by using Fe (II) and Mn (II) and factors that could affect the redox chemistry of chromium. Alternative treatments to adsorb chromium on to low cost materials such as coir, peat, charcoal and wood bark will be studied the adsorption using batch and column flow throughsystem

Chapter 2
Materials and Methods

This chapter describes the materials and methods that were common to all experiments. Materials and methods specific to only one experiment will be discussed in the appropriate chapter.

2.1 Routine methods

All glassware and plasticware used throughout was washed in a 2-5%, solution of Decon 90 chemical cleaner and rinsed 3 times with de-ionised water before being dried overnight in an oven at ~ 80 °C. Deionised water was used to make up all solutions.

2.2 Soil sample preparation

The soil samples were taken to the laboratory, spread out on clean plastic sheet on a bench, roots and stones were removed by hand. The samples were left to dry at laboratory temperature for 7 days. The air-dried samples were sieved through a 2 mm stainless steel sieve. The samples were stored at room temperature in self-sealing plastic bags.

2.3 Measurement of soil pH

The buffer solutions with pH 4 and 7 (BDH chemicals ltd) were prepared from tablets in 100 ml of deionised water.

Soil pH was determined in a 1:2.5 soil: deionised water suspensions by a combined glass-reference electrode and Mettler Delta 320 pH meter (MAFF/ADAS, 1986). The pH meter was standardised with buffer solution of pH 7 and pH 4.

The suspensions were prepared by weighing 10 g sample of each soil into 120 ml screw cap glass bottles and 25 ml deionised water was added to each bottle and the pH was measured. The electrode was then immersed in the bottle and the measurement taken when a steady reading was obtained, after approximately 10 minutes.

2.4 Aqua regia digestion for total chromium concentration

The pseudo total chromium concentration was measured using aqua regia digestion. This technique is widely used for chromium determination in environmental samples and is suitable to determine chromium in most samples even at low concentration. Although aqua regia does not dissolve the whole sample it has become the widely accepted digestion acid for contaminated land (Ure, 1995).

Digestion of soil was done using aqua regia digestion. Aqua regia was prepared by mixing three parts 6M HCl to one part 69% HNO_3.

Soil samples (0.5g) weighed using a four-figure balance, in three replicates. Each sample was placed in a 50 ml beaker and 10ml of aqua regia solution added and beakers covered with watch glasses. The beakers were allowed to stand for at least 12 hours to allow the acid to equilibrate with the soil. The beakers were then placed on the hot plate preheated to 125 °C .The watch glasses were slightly open to remove the brown NO_2 gas evolved during the digestion. The digestion was run for 3 hours until the beakers were clear of brown gas. The beakers were cooled and 10 ml of deionised water were added. Then the digests were filtered with washings using a hardened filter paper Whatman No. 50 into 50 ml volumetric flasks and made up to volume.

2.5 Extractable chromium in soil using deionised water

The water extraction method quantifies soluble forms of Cr (Baes et al.) from soil and waste materials with minimal method-induced oxidation of Cr (III) or reduction of Cr (VI). Chromium was extracted from soil with 50 ml deionised water (James et al., 1995). The concentration of the chromium in the extract was determined with an atomic absorption spectrometry (AAS).

2.5.1 Method

1- Apparatus

Reagent bottles 250ml, 120ml borosilicate glass with plastic cap, and shaking machine.

2- Reagents

Deionised water was taken from the ELGA (model LA613) distillation system.

3- Extraction procedure

5 g of air-dried soil was weighed in to a bottle and 50 ml deionised water added. The bottle was shaken on the end-over-end shaking machine 26 rpm at room temperature (24 °C) for 1h. The soil suspension was filtered through a 125 mm Whatman No.2 filter paper and the filtrate retained for determination of chromium.

2.6 Atomic Absorption Spectrometry (AAS) measurement

In the all experiments the samples were analysed using Atomic Absorption Spectrometry, on a Perkin Elmer 1100B model.

In this set of experiments the maximum absorbance for chromium was obtained under the following condition using acetylene - air flame (Fifield, 1995).

Fuel: 3.5 litre/minute

Air: 8 litre/minute

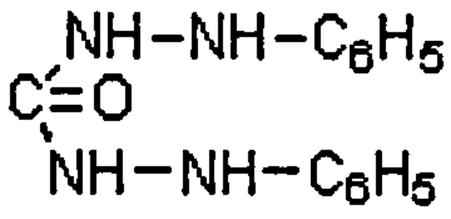
Wavelength: 357.9nm

Detection limit (D.L.) was estimated to be 5 mg/kg for acid digestion and water extract.

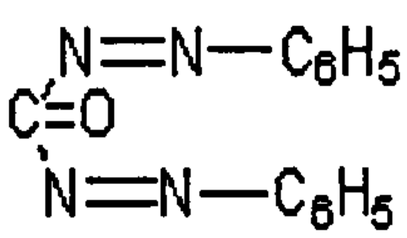
Standard solutions for calibration made by diluting a BDH Spectrosol solution (1000 mg Cr/l). This was diluted to give a linear working range of 0-5 mg Cr/l solutions.

2.7 Manual Colorimetric determination of chromium (VI)

A colorimetric method was used to determine soluble Cr (VI) in soil. The Cr (VI) reacts with diphenylcarbazide (DPC) in acid solution to produce a red-violet colour, stable complex. This process is preceded by a redox reaction, which proceeds in a 2:3 ratio Equation 2.1.



diphenylcarbazide



diphenylcarbazone

2Cr (VI) +3 diphenylcarbazide (PDC) Cr (III) + 3 diphenylcarbazone (DPCO) Equation 2-1

In this way the very reactive Cr (III) is formed in site existence, which is capable of forming a coloured complex with the oxidation product of the reagent Equation 2-2. These reaction products in turn produce a complex with the characteristic colour, which is measured at 540 nm (Tian and Schwedt, 1996).

$Cr(III) + PDCO \rightarrow [Cr(III) - PDCO]^{(3-n)+} + nH^+$ Equation 2-2

2.7.1. Method

1- Reagents

Sulphuric acid 0.5 M prepared by adding 28 ml Analar concentrated (98%) H_2SO_4 to approximately 500 ml deionised water in a 1 litre volumetric flask, allowed to cool and made up to volume.

Diphenylcarbazide solution, 0.25 g 1,5- diphenylcarbazide was dissolved in 50 ml acetone. This solution is only stable for a few days, it was discarding when it became coloured (Sandell, 1959).

Chromium stock solution (1000 mg/l Cr as dichromate) was prepared using analytical grade $K_2Cr_2O_7$ dried in an oven at 105 ^{0}C and cooled in desiccators. 2.829 g were carefully weighted and was dissolved in deionised water, then transferred quantitatively to a 1 litre volumetric flask and make up to the mark.

Chromium standard 5 mg Cr/l, 5 ml of the stock chromium solution was diluted to 1000 ml in a volumetric flask.

2- Calibration

Chromium standards containing 0 - 25 µg chromium were prepared by pipetting 0 to 5 ml of the 5 mg/l standard solution into 50 ml volumetric flasks and diluting to approximately 40 ml then mixing well. 5 ml H_2SO_4 of 0.5 M was added and 1ml diphenylcarbazide, the volumetric flask was made up to the mark and mixed well (Bassett et al., 1994).

The solutions were allowed to stand for 5 to 10 minutes for colour development and the absorbance measured at 540 nm using a UV-visible spectrophotometer (HITACHI-u1100).

Detection limit (D.L.) is estimated to be 1 mg/kg.

3- Samples

Sample containing no more than 25 µg chromium was pipetted into 50 ml volumetric flask and reagents added as described above.

2.8 Oxidation - Reduction of chromium by potential oxidising and reducing agents for soil remediation

2.8.1. Method

1- Reagents

Ferrous sulphate $FeSO_4$ and manganese sulphate $MnSO_4$ were used as reducing and oxidising agent.

2- Extraction procedure

0.5 g of soil was weighed in to a bottle and 0.05, 0.1, 0.15 or 0.2g Fe (II) or Mn (II) added the 3 replicates were run for each. 50-ml water was added and the bottle shaken on shaking machine for 1h. The solutions were filtered through a 125 mm Whatman No.2 filter paper and the filtrate retained for determination of chromium.

2.8.2. Time factors method

0.5 g of soil samples, 0.1 g of $MnSO_4$ and 50 ml of deionised water were added into a bottle. The bottle was stoppered and shaken for 5 h, then left at room temperature for (24, 48, 72h). The samples were shaken for 2 h each time and filtered through a Whatman No.2 filter paper then kept for determination of chromium.

2.8.3. pH factor

Determination of pH buffer curves

0.5 g of sample was weighed and 50 ml of deionised water added then 0.05 M HCl acid was added gradually. After each addition the pH was measured using the pH meter, a steady reading was obtained after approximately 10 min (see Figure 2.1).

To control the pH in this experiment 1 M HCl (0.5, 0.4, 0.3, 0.2, 0.1 ml) was added to 0.5g of soil for different pH from 4 to 8. 0.1 g of Fe (II) or Mn (II) salt was added with 50 ml deionised water and shaken on the shaking machine for 1h, then filtered through a 125 mm Whatman No. 2 filter paper. The filtrate was retained for determination of total chromium by using AAS and Cr (VI) by colorimetric method. Each pH was measured in 3 replicates

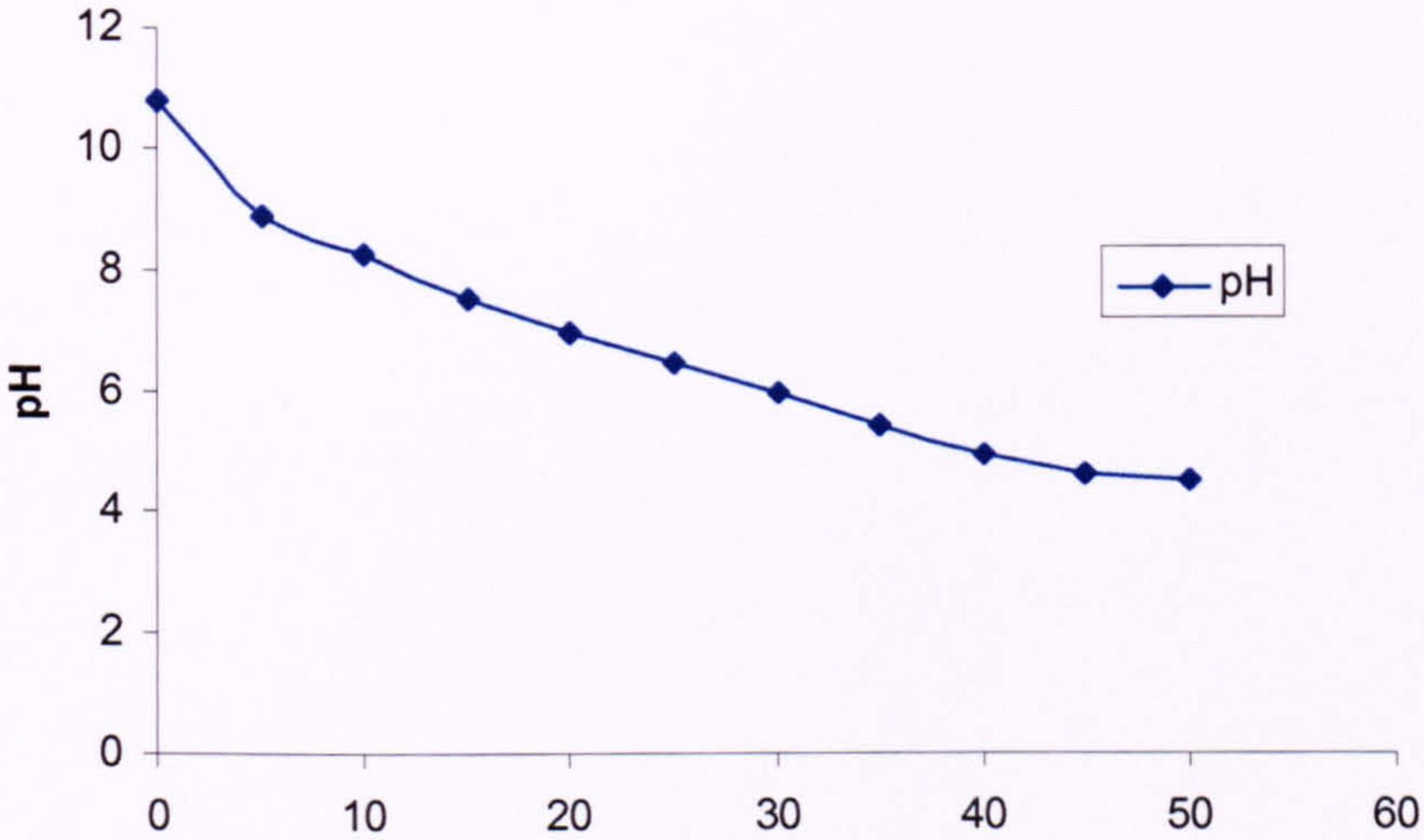


Figure 2-1 Determination of pH buffer curves

2.9 Sorption of Cr (III) and Cr (VI) by different sorbent materials

The adsorbents used in batch experiments were designed to investigate the adsorption - desorption behaviour of both cationic Cr (III) and anionic Cr (VI). The development of the method is outlined in Chapter 6.

2.9.1. Materials

The material used, bone charcoal, wood bark, peat and coir, are described in Chapter 6 (Section 6.2.2). Solution of Cr $(NO_3)_3.9H_2O$ (AR), $K_2Cr_2O_7$ (AR) and KNO_3 (AR).

2.9.2.Method of batch experiment

2.9.2.1. Standard metal solution

Metal solutions were made using ANALAR reagents throughout. For chromium solution a specific mass as salt was weighed to make a stock solution with subsequent dilutions for the range required. Hydrated salts were not dried. A series of solutions of different chromium concentration were made by dilution of a stock solution (typically 2000 mg Cr/l). The chromium concentrations ranged from 5 to 800 mg Cr/l made up with 0.1 M KNO_3 to control the ionic strength.

To have 2000 mg chromium in 1 litre weigh out 15.392 g of chromium nitrate or 5.66 g of potassium dichromate was weighed into a glass beaker on a four-figure top pan balance

before being dissolved in deionised water and than transferred with several washings into a volumetric flask where it was made up to the mark with deionised water.

2.9.2.2. Standard experiment to obtain a sorption isotherm

1g of sorbent was treated with 50 ml of metal solution of concentration range 5-800 mg/l, in triplicate, in 100ml glass bottles, and then shaken in an end-over-end shaker for 60 minutes at room temperature. Immediately the bottles were removed from the shaker the solution was filtered through Whatmans No.2 filter paper (125mm) and the resulting filtrate collected in plastic bottles for storage until analysis. For desorption 47ml of solution was decanted, and to the 3 ml remaining 50ml of deionised water was added and the slurry again shaken for 60 min, after that the slurry was filtered and the samples prepared for analysis using Atomic Absorption Spectroscopy (see Section 2.4).

The equilibrium solution concentration and initial solution concentration were measured by AAS, with any dilution being carried out where necessary to bring the concentration of the samples in accordance to the linear range for chromium in the AAS. The values obtained were then used to calculate the amount of metal sorbed per gram of sorbent as follows using the principles of mass balance.

Example calculation

If $m.X = V(C_i - C_e)$ then **Equation 2-3**

$X_{ads} = (V(C_i - C_e)) / m$ where **Equation 2-4**

X_{ads} = mass of metal adsorbed (mg/g), V = volume of metal solution added (litre), C_i = initial metal concentration (mg/l), C_e = equilibrium solution concentration (mg/l) and m = mass of sorbent (g).

To calculate the desorption amount of metal the values obtained were applied to the Equations below:

$$T = X + (C_e \times V_r) \qquad \textbf{Equation 2-5}$$

$$X_{des} = T - (C_d \times V_t) / m \qquad \textbf{Equation 2-6}$$

X_{des} = mass of metal desorbs (mg/g), T = total metal concentration at start of desorption (Odukoya et al.), C_d = desorbed metal concentration (mg/l), V_r = volume of remain solution (litre), V_t = volume of total amount of solution of desorption (litre), m = mass of sorbent (g).

The data from mass-balance equations allowed an adsorption isotherm to be plotted. An adsorption isotherm describes the relationship between the amount, or concentration of adsorbate that accumulates on adsorbent, and the equilibrium concentration of dissolved adsorbate. The Langmuir equation has been applied to the data extensively (Equation 2-6). This has enabled a theoretical value (X_{max}) to be obtained for the amount of metal that is possible to be sorbed by sorbents. Within this value there is of course variability (as with analytical measurement).

$$C_e/X_e = 1/X_{max}b + C_e/X_{max} \qquad \textbf{Equation 2-7}$$

X_{max} and b = Langmuir constants

C_e = the concentration of adsorbate after equilibrium (mg/l)

X_e = amount adsorbed at equilibrium (mg/g)

The percentage removal of chromium was calculated as flows Equation (2-8):

$$\%\ \text{Removal of Cr} = (C_i - C_e) \times 100/Ci \qquad \textbf{Equation 2-8}$$

2.10 Column method

Columns were constructed to compare results from batch systems while continuing to work towards the aim of determining best-suited condition for real-world systems.

2.10.1 Column Set up

Glass columns were obtained of length 300 mm and internal diameter of 27 mm. They were open at one end tapered at the other. Plastic tubing was attached to the tapered end and directed to a collecting vessel. The column was packed with a small amount of glass wool – enough that when compacted it provided a 20 mm barrier between the charcoal or wood bark and small amount of acid sand the end of column as a filter to ensure no fines were washed through the system. The column was then packed with a certain mass of sorbent (bone charcoal and wood bark) as determined to examine specific column conditions. This was added as wet slurry by a filter funnel after a small amount of water had been added to ensure even settling. After packing, the column was washed through with 2-3 bed volumes of deionised water overnight to 'wet' the column. This was important to ensure that all air was expelled between and within the sorbent particles before the experiment began since air pockets inside the column could result in channelling, which would lower the bed utilisation.

2.10.2 Column Experimental procedure

Metal ion solutions were prepared in a similar way to that outlined in Section (2.9.2.1). In this case large volumes were required for laboratory based column work. 1 litre of chromium stock solution was placed in a reservoir above the glass column containing the amendment being tested. An air leak tube was used in the reservoir column to allow air circulation. The chromium solution was transferred to the amendment column via a swan neck T piece. The flow rate was adjusted by using gravity. The metal solution was passing vertically through down the column and samples collected at time intervals suitable for the flow rate until the metal concentration was likely to have achieved breakthrough at the end of the column according to previous batch work.

The later column system was designed with a peristaltic pump calibrated to a specific flow rate to give a particular linear velocity was used to ensure a constant flow of metal solution. The metal solution was pumped horizontally through the column. A more detailed description of this system will be given in Chapter 6 (see Figure 6.1).

Chapter 3
Survey of Chromium Contamination in Soil in Glasgow

3.1. Introduction

Historically, solid waste from the processing of chromite ore (Hursthouse et al., 2003) has been disposed of at a number of sites in Rutherglen and Cambuslang, in the southeast of Glasgow (see Saction 1.5). This waste came from the White's chromium processing factory at Shawfield, Rutherglen, which operated for about 150 years from 1820 to 1968. It was one of the worlds largest producers of chrome, with an output of approximately 6,000 tons of dichromate recorded for 1880, rising to approximately 30,000 tons by the time of its closure in 1968 (Farmer et al., 1999). Its products met demand for chromium compounds required for metal finishing, tanning and pigments. This factory used the high lime process (Darrie, 2001), which involved roasting the chromite ore with alkali and diluting the melt with lime. In the White's factory, the ground chromite was roasted at 1150 °C with K_2CO_3 up to 1880, after which Na_2CO_3 was also used, and after 1918 sodium carbonate alone was used. It was also necessary to add a diluent to the melt to ensure that sufficient air was present to drive the oxidation of chromite to chromate. Initially CaO was used, but this was replaced by dolomite ($CaMg(CO_3)_2$) in the early 20th Century (Farmer et al. 1999). It is estimated that the high lime process produced approximately 2 tons of waste for each ton of dichromate produced, and so over the lifetime of the White's factory it has been estimated that 2.5 million tons (dry weight) of waste were produced. The exact nature of the wastes produced varied depending upon the production practices in the factory at various times, and these are described by Farmer et al. (1999). Overall however

the wastes were alkaline and contained 1 – 2 % chromium oxide and some of this chromium was in the hexavalent form.

The wastes were initially dumped on sites adjacent to the factory, but as these became filled other sites in the locality were landfilled with the waste material. This has led to the current concern about chromium contamination of the environment, and the possible health risks to humans, in this area. The problem came to public attention early in 1991 (Eizaguirre-Garcia et al., 1999) when redevelopment in this area, and in particular the building of an old peoples' home in a corner of a local park, revealed the presence of chromium waste buried underground. Further examples were found in other areas, for example Cr (VI) was discovered leaching into the Merry Burn at Muirend about 5 km from the White's site (SEPA, (1999 -2000)). Public concern arose due to reports of an excess incidence of leukaemia for some areas of southeast Glasgow and the fear that this was linked to the presence of chromate in the environment. The report of Eizaguirre-Garcia et al. (1999) found no evidence of a link between the chromium waste and the leukaemia, but the public concern remained. Furthermore, potential risks to the environment were also raised, with SEPA being particularly concerned about leaching of Cr (VI) into natural waters. Much attention is now focused on the M74 extension, which will pass through some of the most contaminated areas, including Southcroft Park, which was one of the dumping sites adjacent to the factory.

Following the identification of the problem of chromium waste in this area, and the concerns about possible health hazards, a number of studies have been undertaken to quantify the chromium concentrations in soils and sediments in the Glasgow environment (Tables 3.1). These studies showed that Cr concentrations in soils varied considerably, but in areas where chromium ore processing residue (COPR) was found total Cr concentrations were typically many thousands of mg / kg, and in many cases significant amounts of this

Cr were present as Cr (VI). Analysis of river sediment in streams such as the Polmadie Burn that drain the Shawfield area show that it contains high Cr concentrations, and there is evidence that the Cr is transported into the river Clyde itself (Hursthouse, 2001; Hursthouse et al. 2003). Analysis of groundwater, soil pore water and surface water (Table 3.2) has shown that Cr is leached from the soil and that most of the chromium in solution is present as Cr (VI).

Table 3-1 Values reported in the literature for Cr concentrations in soils and sediments in the Glasgow area.

Reference	Sites of the soil and river sediment samples	Cr mg/kg	Cr (VI) mg/kg
(The Director of Environmental Health, 1992)	1. Burnhill Football Ground, Toryglen Road, Rutherglen; 2. Dukes Road Playing fields; 3. Former Eastfield Quarry, Cambuslang; 4. Southcroft Park 5. Industrial Estate, Southcroft Road; 6. Roseberry Park, Toryglen Street 7. 56/82 Dukes Road 8. Rutherglen Cruising Club, Seith Road 9. Boundary Road 10. Quay Road 11. Glasgow Road 12. Seath Road	9400 9600 14856 26150 7850 - 21200 12850 4380 5340 7130 6520 6850 - 13200 6520	3660
(Duncan et al., 1994)	4 trial pits to max. depth of 3m on Boundary Road, Rutherglen	169 - 39300	4 - 2050
(Farmer et al., 1999)	Dukes Road Playing fields (20-40 cm) depth Cambuslang Rutherglen Glencairn Football Ground Soil terracing (0-50cm) Rutherglen and Rosebery Park (5-50 cm)	14700 - 36400 5800 - 25000 8810 - 22500	1250 ±12 290 - 4670 3520 - 8500
(Bewley et al., 2001)	15 unidentified at sites in southeast of Glasgow	Max Mean 13600 1200 35000 3000 23600 2400 1600 200 41600 10200 16900 5800 65100 13900 12900 3600 4400 480 5300 1800 18100 2300 6500 1500 37100 5900 21400 4300 5200 840	Max Mean 13000 1200 5900 630 8700 780 15 7 15600 2900 1700 360 7300 2100 200 67 3700 250 840 280 190 68 1600 150 10700 1300 <5 <5 4700 510
(Manzur et al., 2001)	15 samples at Southcroft Park	100-31000	20-700
(Graham et al., 2006)	Rosebery Park (10-20 cm)	39000	7934
(Whalley et al., 1999)	Sediment from confluence of Polmadie Burn and River Clyde	3600 - 6600	
(Hursthouse, 2001)	Clyde Estuary White Cart- main river channel sediments	16 - 800	
(Hursthouse et al., 2003)	Surface sediments from River Clyde	7 - 779	

Table 3-2 Values reported in the literature for Cr concentrations in waters in the Glasgow area.

Refere nce	Sites of the water samples	Cr mg/l	Cr (VI) mg/l
Groundwater samples			
(Whalley et al., 1999)	Southeast Glasgow known contaminated with COPR	169	153
(Farmer et al., 1999)	Dukes Road Playing fields	2.4 - 30	2.4 - 30
	Cambuslang Rutherglen Glencairn Football Ground	0 - 15.2	0 - 1.6
	Rutherglen and Rosebery Park	< 0.01	< 0.01
	Myrtle Park	7.4 - 33.3	7.4 - 33.3
(Farmer et al., 2002)	At or near COPR- contaminated site in SE Glasgow and South Lanarkshire	< 0.01 - 91.4	< 0.01 - 81.9
(Graham et al., 2006)	Southcroft Industrial Estate 2.8 m depth	3550	3425
	Rutherglen Glencairn Football Ground 2.54 m depth	55.8	0.13
	Rosebery Park 2.93 m depth	<0.01	<0.01
Pore water samples			
(Whalley et al., 1999)	White Cart to the main Clyde channel (1.5- 11.5 cm)		10 - 30
(Hursthouse et al., 2001)	Clyde estuary	2 - 70 Mean 30	
(Farmer et al., 2002)	At or near COPR- contaminated site in SE Glasgow and South Lanarkshire	7.38 - 125	7.01 - 79.5
(Hursthouse et al., 2003)	(1.5-12cm)	Max. Min. Mean	
	White Cart – Netherton	70 24 49.05	
	Paisley Harbour	54 10 32.7	
	Erskine Bridge	20 2 9.9	
	Woodhall	58 22 38.35	
Surface water samples			
(Whalley et al., 1999)	Stream (Polmadie Burn) at the confluence of Polmadie Burn with the Clyde River	3.1 - 6.2 1.1	3.1 - 6.2 1.1
(Duncan et al., 1994)	Boundary Road, Rutherglen	64	
(Farmer et al., 1999)	Malls Mire Burn and at Richmond Park	0.2 - 6.5	0.2 - 6.5
(Farmer et al., 2002)	Malls Mire Burn	0.45 - 6.28	0.4 - 6.51
	River Clyde	0.11	0.16
(Hursthouse et al., 2003)	Clyde estuary	2 - 70	

3.2. Aim of the work in this chapter aim

The overall aim of the work described in this chapter is to assess the dispersal of Cr in the Glasgow environment. The studies reported in Table 3.1 show that 'hotspots' of high Cr concentration are found associated with areas where chromium ore reprocessing residue was dumped. These act as sources of contamination in the 'source – pathway – receptor' model discussed in Chapter 1. As stated above, the main receptors that could potentially be at risk are humans and the environment, especially groundwater and surface waters. In the first case the risk of inhalation or ingestion due to blowing of high chromium dust or soil is a major factor that could adversely affect human health and forms the basis of the concerns regarding leukaemia described above. Thus the first aim of this work is to assess the dispersal of Cr from the main dumpsite in Rutherglen and its deposition in surface soils, and to try to identify a background concentration that can be used as a benchmark for contamination. The second aim is to assess the risk to natural waters by quantifying the Cr (VI) concentration in the soils. Such quantitative information can then be used in the development of remedial treatments, which form the basis of subsequent chapters. The aim of these treatments is to break the pollutant linkage pathway between source and receptor.

This work has application worldwide and not merely in Glasgow. The United States Environmental Protection Agency identified Cr as the second most common metal, after lead, present on Superfund sites in the USA (USEPA United States Environmental Protection Agency, 2000). Darrie (1999) states that high lime extraction processes are still commonly used in many countries, especially in eastern Europe and Asia, and account for almost 40% of the estimated annual world production of sodium dichromate of 740 kT in the year 2000.

3.3. Locations of sampling sites

Soil samples were collected from a known dumpsite at Shawfield in S.E Glasgow/ Rutherglen. An area of approximately 200 m^2 was selected for study immediately adjacent to a football pitch, Southcroft Park (see Figure 3.1). Further samples were taken from a grassed recreation ground adjacent to the dump site that lay on the other side of a railway line to the south of Southcroft Park. The soil was mostly sampled to a depth of 10 cm, but on the recreation ground some subsoil samples from greater than 10 cm depth were taken. The samples are described in (Table 3.3).

Sixe samples from the topmost 10 cm depth were collected over the transect across S.E. Glasgow, and ten samples were collected from the top 10 cm on grassed soil transect across North- West Glasgow (Figure 3.2 and Table 3.3). The soils samples were prepared for analyses as described in Section (2.2).

Table 3-3 Description of soil samples.

Sample Number	UK ordnance survey Grid Reference (Grid Square NS)	Description of samples
The Cr dump site Southcroft Park		
1	607620	Bare areas on Cr dump site
2	607620	Beside railway on Cr dump site
3 4 5 6	607620	Bare areas beside railway
7	607620	Cr dump site
8	607620	Yellow material, Cr dump site
9 10	607620	Yellowish white material, Cr dump site
Grassy area recreation ground		
11	608619	Grasses area 6m from fence
12	608619	Surface soil sample
13	608619	Auger sample below 10cm depth 6m from fence
14	609619	Surface soil grasses area 6m from fence
15	609619	Open grassed area from railway side
16	608619	Surface soil 25m from fence on the other side of footpath
17	608619	Surface soil
18	608619	Auger sample below 10cm depth
19	607619	Old fence area surface sample
20	607619	Auger sample below 10cm depth
21	606619	Football area surface soil at fence
22	606620	Surface soil of tree growth on the railway side
23	606620	Auger sample below 10cm depth
Transect across S.E Glasgow		
24	610621	River side on site of former factory
25	609632	Poplin St. North of River Clyde opposite Cr site
26	617610	Limeside Avenue Park near known Cr dump
27	605608	Kings Park Avenue
28	587594	Linn Park
29	573596	Open grassed area, Muirend
Transect N.W Glasgow.		
30	568665	University of Glasgow South front of Main Building
31	567667	University of Glasgow behind Kelvin Building
32	567670	University of Glasgow from Lilybank Gardens
33	558664	Yorkhill
34	548671	Broomhill
35	547675	Jordanhill
36	564684	Maryhill
37	557696	Dowsholm
38	554702	Sport centre, Garscube
39	552703	Near River Kelvin, Garscube

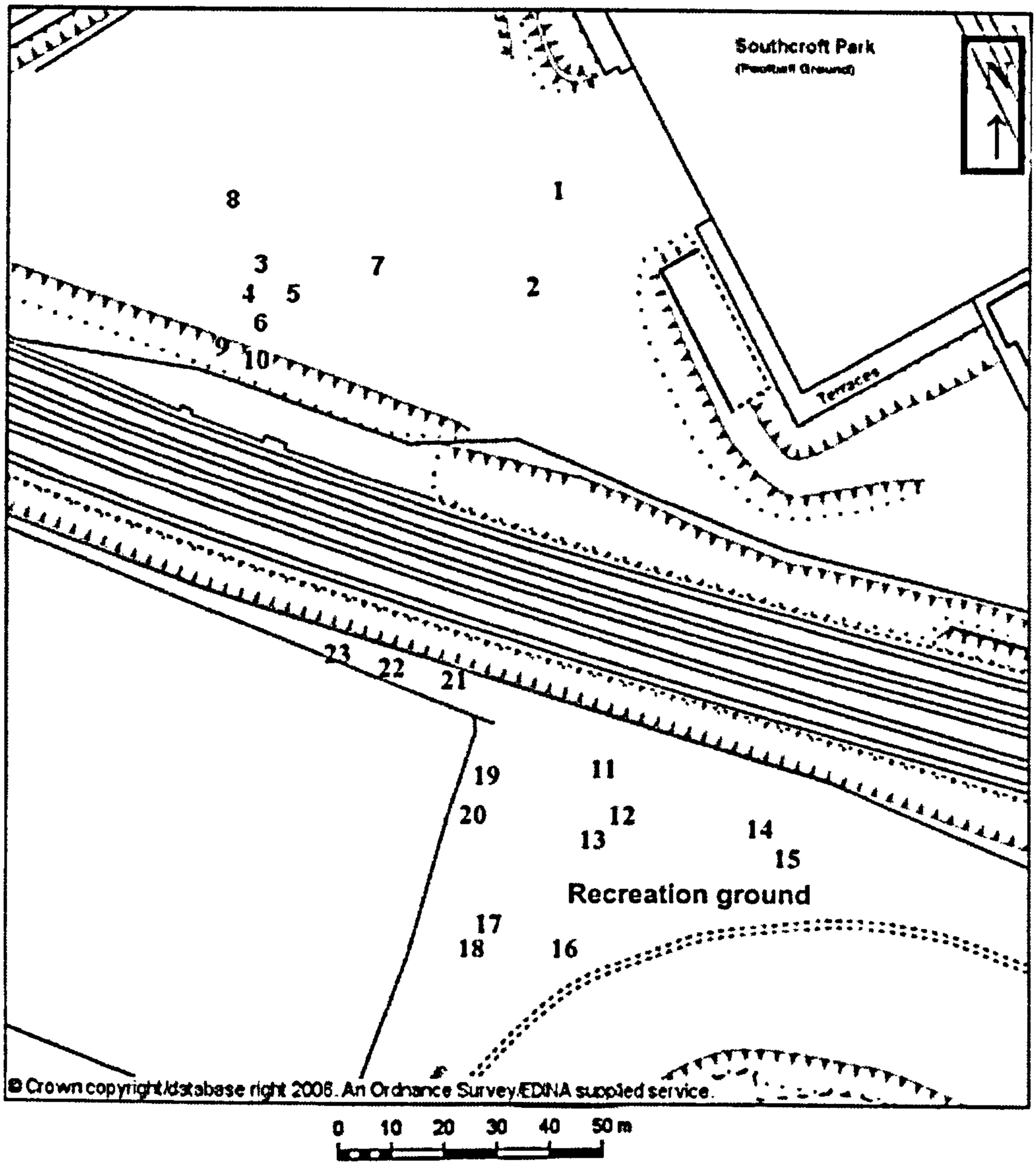


Figure 3-1 Sampling site at Southcroft Park and adjacent recreation ground

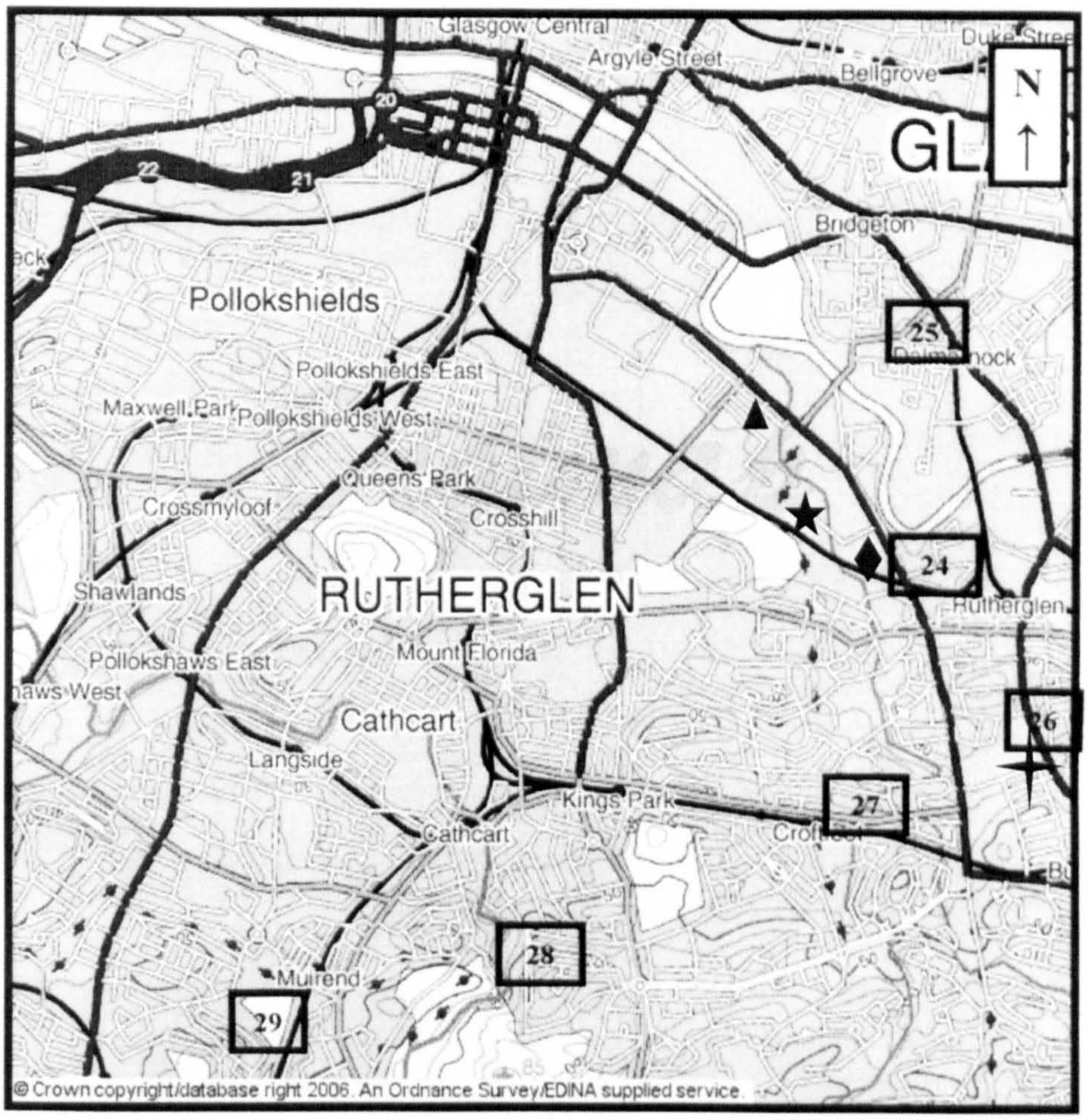


Figure 3-2 Sampling site transect across South-East Known Cr dump areas:

Southcroft Park.

Takecare home and Rutherglen Maternity Hospital

Southcroft Industrial Estate

Roseberry Park

29 **Clarkston Rugby Clubs, Muirend**

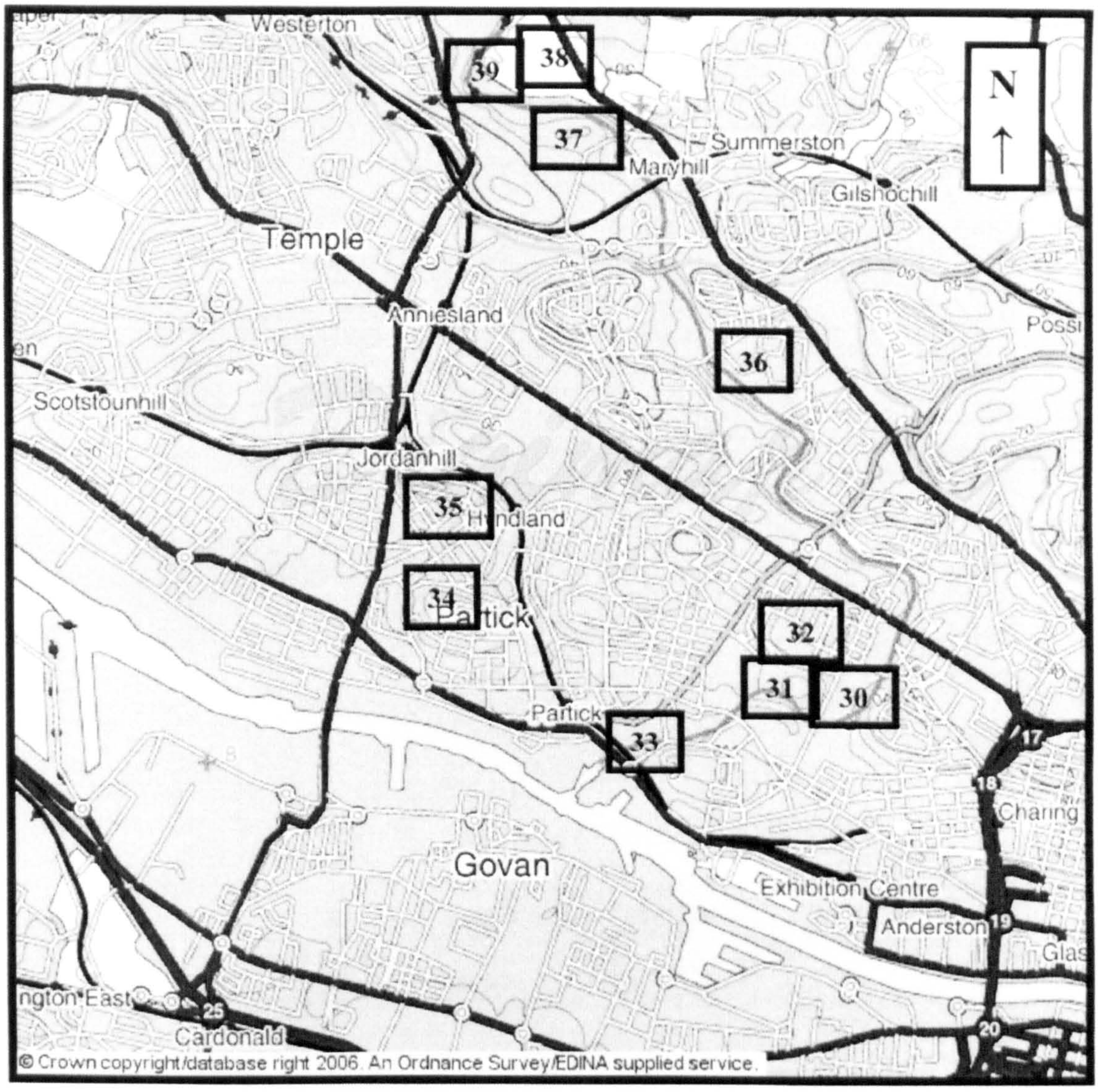


Figure 3-3 Sampling sites across North- West Glasgow
No known Cr dump sites

(a)

(b)

Figure 3-4(a) Southcroft Park. Picture (b) glencairn football pitch.

(a)

(b)

Figure 3-5 (a) at dumpsite adjacent to the railway. (b) yellow material, Cr concentration 6,000-8,000 mg/kg.

(a)

(b)

Figure 3-6 (a) the recreation ground adjacent to dump site. (b) near to River Clyde, Cr concentration 544 mg/kg

(a)

(b)

Figure 3-7 (a) Sample site 29, Muirend, Cr concentration 630 mg/kg. (b) transect N.W Glasgow at River Kelvin, Cr concentration 30 mg/kg.

3.4. Materials and methods

3.4.1. pH measurement

The pH was measured in water at a solution to soil ratio of 2.5: 1 method of pH measurement (see Section 2.3).

3.4.2. Acid digestion

The pseudo-total chromium concentration in the soil samples were measured using aqua regia digestion (Section 2.4) and determined by using single beam atomic absorption spectrometer, zeroed with aqua regia blank and standardised with the 1-5 mg/kg Cr standards.

3.4.3. Water extract

soil samples 1-23 and others that had a total Cr concentration >100 mg/kg were extracted with deionised water (section 2.5). Total water extractable Cr was measured by AAS (Section 2.6) and Cr (VI) by the 1,5- diphenylcarbazide method (Section 2.7).

3.5. Results

The results of total chromium concentration measured by aqua regia digestion and the pH of soil from the sites are presented in Table (3.4). The pH of soil samples from chromium dump was between pH 8–10. The total chromium concentrations for the dumpsite were between 1800 -94000 mg/kg (samples 1-10). Measurable amounts of water extractable

chromium were found in most of the samples from the dump site (Table 3.5), AAS was used to measure total water extractable Cr and colorimetric analysis was used to quantify Cr (VI). Total water extractable chromium was entirely Cr (VI), as confirmed by the agreement between the AAS and colorimetric measurements.

The samples from the recreation ground (11-23) have a variety of total chromium concentrations. Sample 14 had 2300 mg/kg Cr, while samples 19 and 20 were below the detectable limit. In some cases subsurface samples contained more Cr than the surface soil above them (eg. Samples 22 (0- 10 cm) and 23 (>19 cm)). The pH in this site was reasonably uniform between pH 7 to 8. Very low water soluble chromium concentrations were found in the soils from the recreation area all being below the detectable limit for the colorimetric analysis (Table 3.5).

Samples 24 and 29 from transect in S.E Glasgow had high chromium concentration (550 and 630 mg/kg). Total water soluble Cr and Cr (VI) concentrations were below detectable limit for these samples. Samples 25 to 28 had Cr concentrations of approximately 60 mg/kg. The chromium concentrations in soil samples 30-39 from the transect in N.W Glasgow were all approximately 30 mg/kg. The pH ranged from 5 to 8 at sites across S.E and N.W Glasgow (Table 3.4).

Table 3-4 The total chromium concentration of soil samples by aqua regia digestion and pH (n = 3)

Samples	Total conc. Cr (mg/kg)	RSD%	pH
The Cr dump site Southcroft Park			
1	9400	5.6	8.0
2	5400	5.8	8.6
3	1800	13	9.3
4	2400	7.9	9.3
5	3300	19.4	9.2
6	3000	18.8	9.5
7	2900	14.3	10.0
9	8000	2.3	9.1
10	6600	15.8	9.0
Grassy area recreation ground			
11	34	47	8.2
12	75	40	7.7
13	130	43.8	7.9
14	2300	5.6	7.8
15	1320	1.6	7.1
16	21	9.2	7.2
17	63	6.35	7.4
18	38	28.9	7.3
19	B.D.L	___	7.1
20	B.D.L	___	7.0
21	100	9.8	7.2
22	32	21.9	7.3
23	132	22.7	7.4
Transect across S.E Glasgow			
24	550	9.5	8.0
25	63	25.4	6.4
26	68	11.2	6
27	63	32.4	6.3
28	58	8.6	7.1
29	600	12.8	6.7
Transect N.W Glasgow			
30	32	9.4	4.9
31	31	10.6	6.5
32	29	3.8	5.6
33	35	2.3	5.9
34	33	1.5	6.1
35	33	1.5	5.7
36	28	6.4	6.2
37	32	6.7	6.2
38	27	9.6	6.2
39	29	3.1	6.0

B.D.L = below detectable limit

Table 3-5 Concentration of water soluble chromium in soil samples from table 3.2 with total Cr > 100 mg/kg (n = 3)

Sample	AAS measurement Total water extract Cr conc. mg/kg	RSD%	Colorimeter measurement Cr(VI) conc. mg/kg	RSD%
The Cr dump site Southcroft Park				
1	24	12.5	24	8.3
2	42	16.6	43	16.3
3	3	2	B.D.L	
4	11	4.5	12	5
5	8	11.25	9	8.8
6	48	6.25	51	0.2
7	5	20	B.D.L	
9	1200	3.5	1200	3.6
10	900	3.7	980	2.8
11	2	30	B.D.L	
Grassy area recreation ground				
12	3	50	B.D.L	
13	3	16.6	B.D.L	
14	2	30	B.D.L	
15	B.D.L		B.D.L	
16	8	112.5	B.D.L	
17	2	25	B.D.L	
18	3	20	B.D.L	
19	B.D.L		B.D.L	
20	B.D.L		B.D.L	
21	3	20	B.D.L	
22	2	25	B.D.L	
23	2	30	B.D.L	
Transect across S.E Glasgow				
24	B.D.L		B.D.L	
Transect N.W Glasgow				
29	B.D.L		B.D.L	

B.D.L = below detectable limit

3.6. Discussion

3.6.1 *Dumpsite at Southcraft Park (samples 1-10)*

The results of Southcroft Park at dump site were total chromium concentrations between approximately 2,000 and 10,000 mg/kg with a mean of 4760 mg/kg. There are several previous studies covering the same area in S.E Glasgow with known chromium contamination. Bewley (2001) investigated 15 unknown sites in S.E Glasgow known to be high in Cr (VI) and found a maximum total chromium concentration of 65000 mg / kg and a mean of 4000 mg / kg. Manzur (2001) studied 15 soil samples at Southcroft Park and reported chromium concentrations between 100 - 31000 mg / kg. It is apparent that these sites are very heterogeneous. The variations are due to the different amounts of COPR in the samples, and the method of sampling. The samples in this study were mostly in the top soil (0 - 10 cm), and taken at random, while Farmer (1999) studied chromium concentration at the contaminated sites in S.E Glasgow in specific soil layers at different depths. These soil samples were classified depending on the soil colour. For example, from samples taken at 5- 8 cm depth, a purple nodule contained 22,000 mg Cr/ kg, a pink layer a mean of 8,800 mg Cr/ kg and an orange layer a mean of 16,700 mg Cr / kg. It should be noted that the sampling techniques in this work as mentioned above was not the same as the other people work. We were looking for the level of chromium distribution at the dumpsite but they were looking for the specific materials, this is the reason for the wide variety and the heterogeneous of chromium values at this site.

The agreement in water extractable Cr concentrations between the AAS and colorimetric measurements confirms that total water extractable Cr was entirely Cr (VI) at Southcroft Park dumpsite. Several works have identified significant concentrations of hexavalent

chromium extended to different depths on sites in S.E Glasgow, (Manzur et al., 2001) had phosphate extractable Cr (VI) concentrations in the range 20 - 700 mg / kg and Farmer et al., (1999) measured Cr (VI) at different depth using the Na_2CO_3 extraction. For example, Cr (VI) concentration from samples taken at 20 - 40 cm depth had a mean of 1250 mg Cr (VI)/ kg, samples from 0 - 50 cm depth had range of 290 - 4670 mg / kg and samples taken from 8 - 15 cm had a mean of 8500 mg / kg.

There is evidence that chromium is leaching from the dumpsite to the groundwater and ultimately, into the River Clyde. Data from Scottish Environment Protection Agency SEPA (1999 - 2000) found that chromium is detectable in measurable concentrations up to approximately 0.025 mg Cr/l in the River Clyde at Glasgow Green, which is close to waste dumpsite. The work of Farmer et al. (1999) has led to concern about the leaching of the known toxin Cr (VI) into surface water (0.2 - 6.5 mg Cr /l) and ground water (7.4 - 33.3 mg Cr/ l). Walley et al., (1999) reported Cr (VI) concentrations of 3.1 – 6.2 mg/l in the Polmadie Burn, which drains the Shawfield area. At the point where this stream joins the River Clyde a total dissolved chromium concentration of 1.2 mg/l was measured, and at points 1 and 4 km downstream a value of 10 µg / l was measured.

3.6.2. Recreation ground (samples 11-23)

The samples from the recreation ground showed a high value of total chromium in samples 14 and 15, which may be evidence of dust blow by wind from the dumpsite across the railway. Otherwise the surface soil samples from this area show no evidence of enhanced chromium concentration. Cr (VI) could not be detected in water extracts of any of the soils in this area. This may be due to the organic matter content being sufficiently high to reduce any Cr (VI) to Cr (III). Two subsurface samples (13 and 23) had a higher chromium concentration than the samples taken above them. It is known that COPR had been dumped

in this area and covered by soil to form the recreation ground. Thus there may be some contamination from this waste.

3.6.3. S.E. Glasgow transect (samples 24- 29)

Samples 24 and 29 from the S.E Glasgow transect had high chromium concentrations, suggesting that these samples were contaminated with chromium waste. Sample 24 was taken from the banks of the River Clyde close to where the factory had been. Sample 29 was from a rugby ground which had been an old stone quarry and which had a known chromium contamination problem. There was evidence of this from the colours of stream water and the surface soil in this site (Figure 3.6). Although samples, 24 and 29 had high values of chromium with acid digestion, they contained no measurable water-soluble chromium. The soils from the transect in S.E Glasgow that were not contaminated had an average chromium concentration of 60 mg/kg, which is perhaps due to a localised background effect of chromium spread around this area.

3.6.4. N.W. Glasgow transect (samples 30- 39)

In contrast, the chromium concentrations in samples from the transect in N.W Glasgow, where there are no known dumps of COPR, had a mean value of approximately 30 mg Cr / kg. In addition, the background of chromium concentration in sandstone has been reported as 35 mg/kg (McGrath, 1995).

Table (3.6) summarises the background levels of chromium contaminants in Scottish soils in mineral surface horizons in the Giffnock and Darleith soil series (Paterson et al., 2003) Although this area has not been mapped, the Giffnock Series is known to be a common soil in the southern part of Glasgow (Mitchell B.D., 1956; Mitchell and Jarvis, 1956). Table

(3.7) summarises average values for chromium concentration in top soils world wide as well as in the UK and U.S.A.

Table 3-6 The background levels of chromium concentration in tow Scottish soil series

	Cr mg/kg	
	Darleith Series	Giffnock Series
Median	62.9	36.2
Lower quartile	44.4	32.9
Upper quartile	97.4	49
No of samples	11	13

Table 3-7 Chromium concentration in top soils in some countries

Location	No. published	No. of samples	Cr mg/kg	Reference
World	13000		84[a]	(Ure and Berrow, 1982)
Scotland	2944	4122	60[b]	(McGrath, 1995)
England, Wales		6000	34[b]	(McGrath, 1995)
U.S.A			20-85[c]	(McBride, 1994)

a Average
b Geometric mean
c Range of means.

3.7. Summary

The data reported in this chapter confirm the chromium concentrations in COPR and COPR contaminated soils that have been reported in previous studies (Table 3.1). they also confirm the risk to natural water due to potential leaching of Cr (VI) (Table 3.2). Background concentrations of 60 mg Cr / kg in soils from S.E Glasgow and 30 mg Cr / kg in soils from N.W. Glasgow have been suggested. This may reflect an enhanced input of Cr in soils in SE Glasgow due to the influence of COPR dumps, although natural geologised variation may also be a factor.

Chromium contamination from the industry waste continues in countries such as China, Russia, Kazakhstan, India and Pakistan (Darrie, 2001). Therefore there is a need for more effort to protect the environment. The chromium concentration was very high at contaminant site and above the Contaminated Land Exposure Assessment (CLEA10) and Interdepartmental Committee for the Redevelopment of Contaminated land (ICRCL) guidelines values for the park and open space (see Section 1.6) (DEFRA, 2002c). Therefore, it is necessary to find suitable remediation strategies for chromium contamination, as will be developed in the next chapters.

Chapter4

Remediation by Oxidation - Reduction Strategies for Chromium Contaminated Soil

4.1 Introduction

Chromium and its compounds are widely used in industry by various activities (see Chapter 1, Section 1.3.2.2). The effluents and wastes from these industries contain both Cr (VI) and Cr (III) ranging in concentration from tens to thousands of mg/kg. Chromium has been released to the environment via poor storage during manufacturing or improper disposal practices (USEPA, 2000). From the previous chapter the total chromium concentration at the contaminated site studied was 1000-10,000 mg/kg and Cr (VI) was 10-1200 mg/kg. Since chromium (VI) is known to be toxic and carcinogenic, site remediation is needed in order to reduce the risk to humans and ecosystems.

Chromium exists in a number of oxidation states, the most stable and common forms are Cr (III) and Cr (VI) in natural soil. Chromium (III) exists as cation, it is insoluble and less mobile and is the predominant form in the majority of soils and it is essentially non toxic. Cr (VI) exists as anion; it is more mobile in soil and is considered the more toxic form and is known to be carcinogenic. Chromium (VI) with its high positive reduction potential is a strongly oxidising species, and in the presence of soil organic matter Cr (VI) is reduced to Cr (III). Reduction is more rapid in acid than alkaline soils. Redox equilibria are controlled by Eh; the large positive values of Eh favour the existence of oxidised species and low or negative values of Eh are associated with reduced species. Different oxidation states and chemical forms of the chemical substances exist within specified Eh and pH ranges (see Chapter 1 Figure 1.1).

The traditional chromium contamination remediation methods entail a two step operation that reduces Cr (VI) to Cr (III), and then stabilizes the trivalent form to prevent it from leaching.

Oxidation of Cr (III) and reduction of Cr (VI) are reactions that may control the valence state and mobility of Cr at contaminant sites. Knowledge of these soil chemical transformations could be used effectively to predict the mobility of Cr in soil-water systems, and to remediate Cr (VI) enriched soil via reduction processes that minimize the chances of re-oxidation of the newly reduced Cr (III). A seesaw metaphor represents the dynamic, undulating nature of oxidation- reduction reactions of Cr (III) and Cr (VI) in soil (Association., 2002; ICRCL, 1987; James, 2001). One key issue that complicates these remediation efforts is the possibility that Cr (III)-to-Cr (VI) oxidation by manganese (III, IV) (hydr) oxides occurs in soils, a discovery made by Bartlett and James in (1979).

Developing such remediation by reduction strategies is a complex and controversial issue because Cr (VI) does not always readily reduce to Cr (III) and can exist over an extended period of time. The rate and extent of Cr (VI) reduction is strongly dependent on soil conditions.

Clean up of Cr (VI) contamination in soils using reduction reaction is possible in "remediation-by- reduction" schemes employing chemical processes such as zero valent iron (Guha and Bhargava, 2005; Lee et al., 2003), divalent iron (Burge and Hug, 1997), ascorbic acid (Xiang-Rong. et al., 2004) organic compounds (Tokunaga et al., 2003), H_2S (Kim et al., 2001) and microbiologically (Chirwa and Wang, 1997).

4.1. Aim

This chapter will study the affect of Fe (II) and Mn (II) on the redox chemistry of chromium.

4.2. Soil sample

The soil sample available for this study was a white material, which had been used for a previous study, and it was an example of COPR. An initial analysis of total Cr and Cr (VI) was carried out before the soil was used for studying chromium redox chemistry.

4.2.1. Method

Aqua regia digestion was used to measure the concentration Cr in soils see Chapter 2 (Section 2.4) for method used. Water extraction was used to detect the total soluble chromium and Cr (VI) See Chapter 2, (Section 2.5-2.7) for method used.

4.2.2. Analytical results

Table (4.1) summaries the chromium concentration of soil sample. It is obvious that this soil sample had extremely high total water extracted Cr (480 mg/kg) and Cr (VI) 255 mg/kg and so was used for redox study.

Table 4-1 The total Cr concentration via aqua regia and water extractable chromium measured by AAS and Cr (VI) concentration via colorimetric method of soil samples n = 3.

	Cr conc. mg/kg	RSD%
Total Cr by Aqua regia digestion	16670	12
Total Water extract Cr	480	11.5
Cr (VI) in water extract by Colorimetry	255	17

4.3. Oxidation- Reduction reaction of Cr with Fe (II), Mn (II)

A waste sample with an extremely high Cr (VI) concentration (255 mg/kg) was used to study the effect of Fe (II) and Mn (II) salts on the redox chemistry of Cr (VI) and Cr (III) and their potential to remediate the chemical waste.

The oxidation and reduction reactions of Cr in soil and natural water are dependent on the presence of oxidants and reductants. The possible reduction of Cr (VI) by Fe (II) to convert the anionic soluble and toxic form of Cr (VI) in soil to cationic less soluble Cr (III) was studied by (Bartlett and James, 1979; James, 2001; Perez-Benito and Arias, 2001). The main oxidants of Cr (III) to Cr (VI) in soils are Mn oxides (Bartlett and James, 1988). Bartlett and James (1979) studied the behaviour of oxidation of chromium in soil by Mn (III) or (IV) preduced by oxidation of Mn (II), which serves as electron acceptor in the reaction. Manganese dioxide was given a primary consideration for the oxidation of trivalent chromium to hexavalent chromium (Katz and Salem, 1994); (Kim et al., 2002).

4.3.1. Method

The method of extractable chromium from 0.5 g soil with added different amount of Fe (II) and Mn (II) was described in Chapter 2 (Section 2.8.1). The total chromium concentration in solution was determined by using AAS. The chromium (VI) concentration was determined with the colorimetric method.

4.3.2. Results and discussion

Total water extractable chromium concentration [Cr (III) plus Cr (VI)] and chromium (VI) concentration (mean of 3 replicate) were measured following different additions of Fe (II) and Mn (II).

Table 4.2 shows the total water soluble chromium concentration and Cr (VI) concentration following addition of Fe (II) and Mn (II). The total soluble chromium concentration was measured by AAS using both air - acetylene and N_2O – acetylene flames. Because it has been reported that there could be interference by Fe in the measurement of Cr with air-acetylene flame so N_2O- acetylene flame was also used

The measurements of chromium concentration by the two gas mixtures differed by about 2 mg/l, which might be due to the hotter and highly reducing flame of N_2O- acetylene. That difference is much less than the difference in chromium concentration due to the amount of Fe (II) added. There may be some error in the analysis particularly with the multiplication factor required by dilution, which means these numbers are going to vary, but this error is relatively small compared with the variation due to of the addition of Fe (II). In both flames at the highest two levels of Fe addition no soluble Cr was detected. The measuring

of chromium in solution by colorimetric analysis shows that essentially all the chromium measured by AAS in the solution was Cr (VI).

Addition of Mn (II) shows no difference in the concentration of total water soluble chromium with both flames or Cr (VI) concentrations (Table 4.2).

The results of reduction of chromium (mean of 3 replicate) by varied amount of Fe (II) salt are presented in Table (4.3), significant reduction was found with increasing the amount of Fe (II) added (p = 0.000). The total water extractable chromium concentration and chromium (VI) in the contaminated soil was about 1000 mg/kg at the initial addition. By increasing the addition of Fe (II) up to 0.15 g $FeSO_4$ per 0.5 g of soil, the concentration of total Cr and Cr (VI) extracted by water decreased to below the detectable limit. This result shows the beneficial effect of Fe (II) addition to soil considerably decreasing Cr (VI) concentration.

The effect of different additions of $MnSO_4$ salt on total water extractable chromium and chromium (VI) concentration (mean of 3 replicates Table 4.4), confirms that there was insignificant difference between the chromium released and the amount of Mn (II) added. As shown in Table (4.4) the concentration of total water extractable chromium and chromium (VI) were1057 and 1093 mg/kg respectively. Fourfold increase Mn (II) addition resulted in no change in total water extractible chromium or Cr (VI) concentrations.

In contrast, adding the same amount of Fe (II) and Mn (II) on a weight basis found that with Fe (II) there was a gradual decreased in soluble chromium with increasing amount of Fe added, but with Mn (II) soluble chromium had the same value regardless of the amount added from that we start looking to the Mn if there is any other factor could effected such as the contact time.

Table 4-2 Chromium concentration at two type of flame with different amount of Fe (II) and Mn (II) and the Fe concentration

Metal add g	Fe (II) Total Cr in water extract mg/l Air/C_2H_2	Fe (II) Total Cr in water extract mg/l N_2O/C_2H_2	Colorimeter measurement Cr (VI) mg/l	Fe (II) mg/l	Mn(II) Total Cr in water extract mg/l Air/C_2H_2	Mn(II) Total Cr in water extract mg/l N_2O/C_2H_2	Colorimeter measurement Cr (VI) mg/l
0	9	10.5	9.6	BDL	10.5	11.2	11.3
0	9.8	11.6	10.6	BDL	10.2	11	11.3
0	9.6	11.7	10.3	BDL	9.9	10.5	11.3
0.05	5.5	6.4	5.2	BDL	9.7	10.3	10.5
0.05	4.5	5.3	4.4	BDL	9.9	10.4	10.6
0.05	4	5.3	4.2	BDL	10	10.3	10.8
1	0.4	0.6	2.5	BDL	9.6	10.4	10.7
1	0	0	0	BDL	10	10.8	11.3
1	0.1	0.08	0.6	BDL	9	9.4	10
0.15	BDL	BDL	BDL	38.8	10.2	10	11.5
0.15	BDL	BDL	BDL	65	9.6	10.6	10.8
0.15	BDL	BDL	BDL	46	10	10.9	11
2	BDL	BDL	BDL	143	9.6	10.8	11
2	BDL	BDL	BDL	151	9.1	10	10.1
2	BDL	BDL	BDL	189	9.1	10	10.2

BDL= below detectable limit

Table 4-3 Effect of different addition of Fe (II) on Chromium concentration mg/kg extract of soil.

Fe(II) g	AAS Total Cr in water extracts mg/kg Air/C2H2	RSD%	N2O/C2H2	RSD%	Colorimeter measurement Cr (VI) mg/kg	RSD%
0	924 a	1	1095 a	3.5	992 a	2
0.05	451 b	10	544 b	5.5	441 b	7
0.1	15 c	121	22 c	144	10 c	127
0.15	BDL	___	BDL	___	BDL	___
0.2	BDL	___	BDL	___	BDL	___

Numbers with the same letters in column are not significantly different (Tukey LSD test), p > 0.05
n = 3, BDL= below detectable limit

Table 4-4 Effect of varied addition of Mn (II) on Chromium concentration mg/kg of soil. n = 3

Mn (II)	AAS Total Cr in water extracts mg/kg				Colorimeter measurement Cr (VI)	
g	Air/C_2H_2	RSD%	N_2O/C_2H_2	RSD%	mg/kg	RSD%
0	989	4	1057	4	1093	0.4
0.05	953	6	998	5	1028	6
0.1	908	5	972	6	1014	5
0.15	917	2	975	8	1028	2
0.2	883	2	978	3	996	3

4.4. Time factors

The result of the above experiment showed that adding enough Fe (II) could reduce all the chromium, but adding more Mn (II) did not increase the amount of soluble chromium. So this experiment studies the effect of contact time on soluble chromium concentration with Mn (II) added. For the method used see Chapter 2 (Section 2.8.2).

4.4.1. Results and discussion

Release of chromium by addition of Mn could be important. Table (4.4) shows the chromium concentration did not change with the amount of Mn (II) added. On the other hand we want to know whether the effect of time could increase the chromium oxidised.

The changes over time in total water soluble Cr and Cr (VI) following addition of $MnSO_4$ are shown in (Table 4.5).

The concentration of water soluble chromium after 24h was 1980 mg/kg and then clearly the level of soluble chromium was consistent over 48 and 72 h, about 2400 mg/kg.

Because in this experiment we do not have any result less than 24h, the result from the 1h shaking time from the previous experiment (Table 4.4) has been shown and is adopted to the current data on Table (4.5). This suggests that with sufficient time, Mn could increase the amount of chromium oxidised. Also here found the concentration of total Cr was all Cr (VI). This concludes that given sufficient time most of the chromium would be oxidised.

Table 4-5 Effect of time for chromium released (mg/kg) with Mn(II), n = 2.

	Water extractable Cr mg/kg			
Time (h)	A.A.S Soluble Cr	RSD%	Colorimeter measurement Cr (VI)	RSD%
1	972	6	1014	5
24	1980	1.7	1950	5.1
48	2384	2.7	2459	1.7
72	2402	0.3	2412	0.01

4.5. pH Factors

Reducing Cr (VI) to the less mobile and less toxic trivalent state is very difficult at high pH. The pH effects were studied by using Fe (II) and Mn (II) in soil and measuring the total soluble chromium concentration and Cr (VI). Method see Chapter 2 (Section 2.8.3)

4.5.1. Results and Discussion

In this section the relationship between pH and redox chemistry of chromium is studied. Table (4.6) shows the extracted chromium concentrations with different target pH. The statistic shows that p value was $p = 0.108$ for total soluble chromium and $p = 0.42$ for Cr (VI), meaning there is no significant difference between the amount of chromium extracted at different pHs. However the variability was high in this experiment, specially at pH8.

Table (4.7) shows reduction of Cr (VI) by addition of 0.1 g $FeSO_4$ over a range of target pH values. As indicated by p value of total Cr $p = 0.03$ and Cr (VI) $p = 0.003$, pH had a significant effect on reduction of Cr (VI) by Fe (II). At target pH 4 and 5 there was no detectable Cr (VI) in solution. Although the concentration of Cr (VI) decreased from pH 8 to pH 6, the variability in the data means that the results were not statistically significant. The pH values of soil and groundwater have been generally reported between pH 5 and 9. Furthermore, most of the reductants used in the literature were less effective or non – effective in alkaline solution (James et al., 1997); (James, 1994). The rate of reducing chromium increased with decreasing pH below 4 as documented in the literature (Buerge and Hug, 1997). The significant reduction of hexavalent chromium by divalent iron was found to have taken place only with the acidic soils (Eary and Rai, 1991).

As shown in Table (4.8) oxidation of Cr (III) to Cr (VI) by Mn was greater at low pH (Bartlett and James, 1979). More total soluble chromium was measured at lower pH values ($p = 0.004$). The concentration measured at pH 6 and below was significantly greater than at pH 8. The same trend was observed for Cr (VI), but the statistical significance was lessened by the variability in the pH 7 samples. If this is ignored, there is a significant increase in Cr (VI) concentrations at pH 6 and below compared with pH 8. Apparently at target pH 6 and below, there was no more chromium oxidised, meaning that at high pH chromium is more mobile and easily released from soil. From the previous chapter the pH of chromium dumpsite was ranging of 8 - 10, so the pH is an important factor in any remediation.

In same cases the AAS and colorimetric measurement did not agree but in other cases they did. Possible reasons for this are the effect of neutralisation of acid in the colorimetric determination or the time taken to do the colorimetric analysis was delayed because it was not possible to do the two analyses in the same time.

Table 4-6 pH effect on chromium concentration mg/kg without Fe (II) and Mn (II)

Target pH	AAS Total soluble Cr mg/kg replicate	mean	RSD%	Colorimeter measurement Cr (VI) mg/kg replicate	mean	RSD%
	1514			916		
8	2827	2360	31	802	1194	45
	2741			1864		
	1774			1368		
7	1628	1722	5	1308	1351	3
	1767			1377		
	1765			1284		
6	1715	1732	1.6	1467	1387	7
	1717			1410		
	1655			1552		
5	1671	1654	1	1457	1500	3
	1637			1493		
	1633			1608		
4	1615	1645	2	1588	1612	1.6
	1687			1640		

Table 4-7 pH effect on chromium concentration with in 0.1g Fe (II), Numbers with the same letters in column are not significantly different (Tukey LSD test), $p > 0.05$.

Target pH	AAS Total soluble Cr mg/kg replicate	mean	RSD%	Colorimeter measurement Cr(VI) mg/kg replicate	mean	RSD%
	38			32		
8	91	53 a	61	81	51 a	51
	32			41		
	20			20		
7	28	24 a b	17	33	30 a	29
	27			37		
	18			26		
6	10	16 a b	38	14	22 a	35
	22			29		
	5					
5	6	5 b	12	BDL		
	5					
	1					
4	1	9 b	158	BDL		
	26					

BDL= below detectable limit

Table 4-8 pH effect on chromium concentration with in 0.1g Mn(II), Numbers with the same letters in column are not significantly different (Tukey LSD test), $p > 0.05$.

Target pH	AAS Total soluble Cr mg/kg replicate	mean	RSD%	Colorimeter measurement Cr(VI) mg/kg replicate	mean	RSD%
8	1668 1928 1709 1958	1768 a	8	1384 1456 1425 1537	1421 a	3
7	1691 1869 2156	1839 a b	7	1061 1261 1711	1286 a	18
6	2010 2077 2026	2079 b	3	1611 1671 1566	1664 a	3
5	2075 2056 2087	2052 b	1	1640 1629 1584	1611 a	2
4	2067 2131	2094 b	1.5	1591 1657	1610 a	2.5

4.6. Conclusion

The chemical reduction of Cr (VI) to Cr (III) is very important in the remediation of environmental sites contaminated by chromium. Although, the weathering of soil with the time needs to be carefully considered as this could lead to potential re-oxidation of Cr (III). This should be controlled or stabilised to minimise the release of chromium at the treatment soils (Eary and Rai, 1988). Fe (II) is ineffective in alkaline conditions; ((Buerge and Hug, 1997; Deakin et al., 2001).

However, other treatments which have been suggested, such as H_2S, may exhibit toxicity themselves and introduce additional environmental problems (Chulsung et al., 2001)

4.6.1. Fe (II) reduction

Fe (II) could reduce Cr (VI) to Cr (III). Considering the pH factor it has been shown that Fe (II) works more effectively in acid conditions than alkaline. Also, not all the chromium was reduced below a health based maximum allowable concentration, particularly in alkaline media. We know the chromium dumpsite has high pH and this might be one of the difficulties to apply this kind of treatment at this site. The mechanism of Fe (II) reacting with chromium is that Fe (II) is oxidised to Fe (III) (hydr) oxides at the same time Cr (VI) reduced to Cr (III) (Buerge and Hug, 1997; James, 2001). The Fe (II) compounds are the most commonly used reagent in the literature summarised in able 4.8 (Eary and Rai, 1988).

Table 4-9 Summary of Reductants, Conditions, and Efficiencies of Treatment Processes for Removing Cr (VI) from Various Aqueous Wastes Reported in the Literature.

Ref.	Reductant	pH of reduction step	T, °C	Cr product	Efficiency[a]
(Anderson et al., 1984)	magnetite + $FeSO_4.7H_2O$	6-8	nr[b]	$Cr(OH)_3$	1-1.2
(Lancy, 1966)	Fe sulphides	4.5-7	nr	$Cr(OH)_3$	nr
(Butler, 1984)	magnetized Fe particles	2.7-3.5	nr	$Cr(OH)_3$	nr
(Kindl and Atkinson, 1978)	S^{2-} + Fe (II) salt	7-8	40-60	$Cr(OH)_3$	1.7-2.7
	Ferrous mud of (1 mol of $FeSO_4$ + 1.7 mol of NaOH)	10-12	40-60	$Cr(OH)_3$	3-5
(Sakaibara et al., 1979).	Ferrous salt	6-10	40-90	Chromium ferrite	2-100
(Hamano, 1974)	$FeSO_4$	7.5	nr	$Cr(OH)_3$	nr
(Fuji, 1977)	Ferrous salt	4.5-8.5	nr	$Cr(OH)_3$	1.0
(Moring, 1980)	Fe electrode	4.5-5.8	nr	$Cr(OH)_3$	nr
(VEB et al., 1973)	$FeSO_4$ + electrolytic reduction	<3	nr	nr	nr

a Efficiency is defined here in terms of Fe (II) required to produce complete Cr (VI) reduction (3 mol of Fe (II) to 1 mol of Cr (VI)).
b nr indicates quantities not reported

The length of time required to remove aqueous Cr (VI) by various treatment methods is largely determined by the reactivity of the Fe (II) source. Methods of laboratory based studies that use slowly dissolving Fe (II) solids such as magnetite (Anderson et al., 1984), iron sulphides (Lancy, 1966) , or ferrous salt and iron particles require from 15 min to 6 h (Butler, 1984; Kindl and Atkinson, 1978), low pH, and, in some cases elevated temperatures to increase the amount and rate of Fe (II) release to solution. Methods that use highly soluble Fe (II) salts (Fuji, 1977; Hamano, 1974; Kindl and Atkinson, 1978; Sakaibara et al., 1979) such as $FeSO_4.7H_2O$, are reported to produce much more rapid rates of aqueous Cr (VI) reduction, but some of these methods also require that the solutions be heated to 40-90 °C, this is expensive step for an industrial treatment process. Also for some of the treatment methods in Table 4.3, from 2 to 100 times the stoichiometric amount of Fe (II) is reportedly needed to realize complete Cr (VI) reduction (Sakaibara et al., 1979).

Eary and Rai (1988) described the reaction of aqueous Cr (VI) by aqueous Fe (II) by the overall reaction

$$Cr\ (VI)\ (aq) + 3Fe\ (II)\ (aq) \quad Cr\ (III)\ (aq) + 3Fe\ (III)\ (aq) \qquad \textbf{Equation 4-1}$$

Given the stoichiometry of reaction 4-1, it is predicted a ratio of 3.0 mol of aqueous Fe (II) oxidised to 1.0 mol of aqueous Cr (VI) reduced for the pH range 2 -10 in oxygenated solutions. Eary and Rai (1988) indicated that aqueous Cr (VI) reduction by aqueous Fe (II) is nonstoichiometric in highly alkaline solutions and moderately alkaline solutions. Aqueous Fe (II) ions are rapidly oxidised by dissolved oxygen in solutions that have been equilibrated with air-oxygen to aqueous Fe (III) reaction 4-2.

$$Fe\ (II)\ (aq) + \tfrac{1}{4}\ O_2\ (aq) + H^+ \quad Fe\ (III)\ (aq) + \tfrac{1}{2}\ H_2O \qquad \textbf{Equation 4-2}$$

The products of the reduction reaction 1 will be precipitated as hydroxide solids in slightly acidic to alkaline solution (reaction 3) depending on their solution concentration, where X can vary between 0 and 1.

$$X\,Cr\,(III) + (1-X)\,Fe\,(III) + 3H_2O \quad (Cr_X\,Fe_{1-X})\,(OH)_3\,(s) + 3H^+ \quad \textbf{Equation 4-3}$$

Chromium (III) hydroxide solids, including $Cr(OH)_3$ (s) and the solid solution (Cr,Fe)(OH)$_3$ (s), have been observed to precipitate rapidly in moderately acidic to alkaline solution and are expected to be the important solubility controlling solids for dissolved Cr (III) for wide range of pH. The solubility of these solids limits Cr (III) concentrations, between pH 5 and pH 11, to less than the drinking water limit of 10^{-6} M. Fe (II) reducing Cr (VI) to Cr (III) is better in acidic soils than alkaline soil. Weathering could re-oxidise Cr (III) to Cr (VI) so the Cr (III) should be stabilised in soil could be by precipitated chromium as a mixed of chromium (III) – iron (III) hydroxide phase limits total dissolved concentration of Cr (III) at pH values between 5 and 11 (Eary and Rai, 1988), or by adding organic matter to reduce Cr (VI) to the relatively immobile Cr(III), reduction that occurs naturally in most soils (Banks et al., 2006; McGrath, 1995).

(Blowes et al., 1997) found that the effective removal of Cr (VI) by Fe^0 under dynamic flow conditions in porous-reactive walls containing Fe^0 may be an alternative for treating groundwater contaminated by Cr (VI). They were used four types of Fe-bearing solids, siderite [$Fe\,CO_3$], pyrite [FeS_2], coarse-grained elemental iron [Fe^0], and fine-grained Fe^0. The removal mechanism for Cr (VI) by fine-grained Fe^0 and coarse-grained [Fe^0] is through the reduction of Cr (VI) to Cr (III), coupled with the oxidation of Fe^0 to Fe (II) and Fe (III); it is matching mechanism of Fe (II) react with Cr (VI) as mentioned above.

4.6.2. Mn (II) reduction / oxidation

The mechanism of Mn (II) reacting with chromium is more complicated because we have no idea if Mn could react to oxidise or reduce chromium. This is dependent on the soil conditions, Mn concentration and dissolved oxygen. Bartlett and James (1979) indicated that Mn (II) could oxidise to be mixture of Mn (III) and Mn (IV) and then the reverse reaction could happen to re-oxidation Cr (III) to Cr (VI). Apparently this could explain why we have had high Cr (VI) concentration when chromium reacts with Mn (II).

Perez-Benito and Arias (2001) observed that reaction between Cr (VI) and Mn (II) was not reacting in aqueous perchloric acid in the absence of stabilising ligands such as pyrophosphate stabilising ligand for Mn (III) is present in the medium, to avoid the backward reaction [Cr (VI) + 3Mn (II) □ Cr (III) + 3 Mn (III)]. Perez-Benito and Arias (2001) suggested the mechanism of Mn involving three consecutive first electron redox steps is proposed for the reduction of Cr (VI) to Cr (III), in each step a Mn (II) being oxidised to Mn (III), whereas colloidal manganese dioxide might be a key intermediate for the reoxidation of Cr (III) to Cr (VI).

There is some evidence in the presence of Mn (II) that Cr (VI) is reduced to Cr (III) in the human nutrition (Perez-Benito and Arias, 1993; Perez-Benito and Arias, 1998).

From this point, we found that Mn (II) could oxidise Cr (III) to Cr (IV) even at high pH and with sufficient longer contact time. Several examples have been reported in the literature where Mn oxides decrease the solubility of chromium by an oxidation process. (Kim and Dixon, 2002) revealed that the Cr oxidation rate increased with increasing content of reactive manganese (Mn) oxides and decreasing pH of the soils, but the soils

high in Mn-oxides and low in organic matter are able to oxidize chromium (Chung and Sa, 2001).

The mobility of Cr (VI) in soils and natural waters is much higher than Cr (III) because Cr (VI) forms anionic complexes and more soluble compounds. From that Cr (VI) could leach from the soil and be collected for treatment using a bed of amendment materials that could hold chromium, and this method will be studied and developed in Chapter 5.

Chapter 5
Chromium Leaching from Soils

5.1. Introduction

This chapter studies the mobilization of chromium within contaminated soil and its potential for transfer to the ground water. There has been concern about the leaching of the known toxin, Cr (VI). The ground water and streams in the area of this study, which eventually flow into the River Clyde, are heavily contaminated at concentrations of up to 100 mg/l (Farmer et al., 1999; Geelhoed et al., 2003). SEPA (1999-2000) detected chromium in measurable concentrations in the River Clyde at Glasgow Green, which is close to the waste dumpsite (Figure 5.1). That means that chromium was leaching from the contaminated soil to the River Clyde (SEPA, (1999 -2000)).

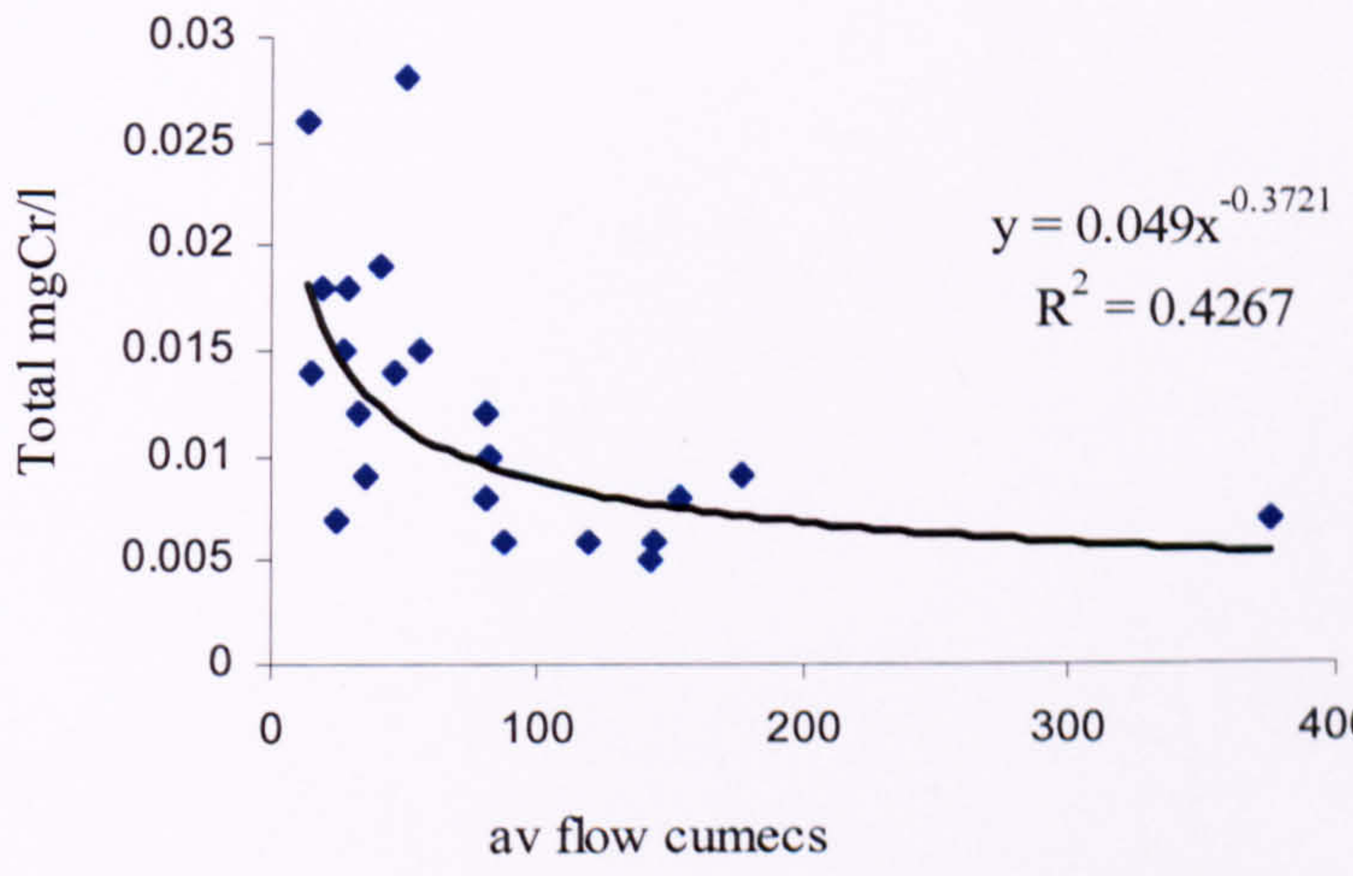


Figure 5-1Total chromium concentration in River Clyde with average flow. Data from Scottish Environmental Protection Agency

5.2. Aim

The aim of this study is to provide information on the leaching characteristics of chromium from the soils. Column and batch experiments were used.

Two heavily contaminated sites (9 and 10) from chromium dumpsite discussed in Chapter 3 were selected for studying chromium release from soil with time and volume of water added. These soils, which contained high concentration of Cr (VI), were mixed thoroughly in a 1:1 ratio to give sufficient material for use in these experiments.

5.3. Batch Water extraction

0.5 g of air dry soil was weighed in glass bottles then 50 ml of deionised water added and left for contact times of 0, 1, 5, 9, 15, 19, 23, 29, 33, and 37 days. It was done in triplicate. The bottles were shaken for 1 h prior to each sampling time and then the soil suspension was filtered through Whatmans No.2 filter paper (125 mm) and the resulting filtrate collected in plastic bottles for storage until analysis using atomic absorption spectroscopy (see Section 2.6).

5.4. Column water leaching

Three glass columns of length 290 mm and internal diameter of 27 mm were used. An adaptor was placed in the top of each column with plastic tubing connecting to a reservoir of deionised water (Figure 5.2). The column was packed with a small amount of glass wool and then a layer of acid washed sand added to act as a filter to ensure that no fines were washed through the system. A small amount of glass wool was added to the top of the sand to act as a barrier between the sand and soil.

The column was then packed with 10 g of air dry soil and flushed with 10 litres of deionised water in 100 ml increments with a flow rate 8 ml/min using gravity. The chromium concentration in each 100 ml sample was measured by AAS.

Figure 5-2 Column leach system

5.5. Result and discussion

5.5.1. ***Batch water extraction***

In the variable contact time batch tests, carried out to release chromium from waste soil, the cumulative amount of chromium released increased with time of contact (Figure 5.3). That shows an initial fast release followed by a much slower release (Figure 5.3). These values equate to 1200 mg Cr/kg after one day and 1840 mg Cr/kg after 37 days, over twice the initial amount of chromium released. In chapter 3 it was reported that the chromium concentration in samples 9 and 10 were 1200 and 900 mg Cr/kg respectively measured by batch extraction for 1h, which is matching approximately the chromium released in this batch experiment.

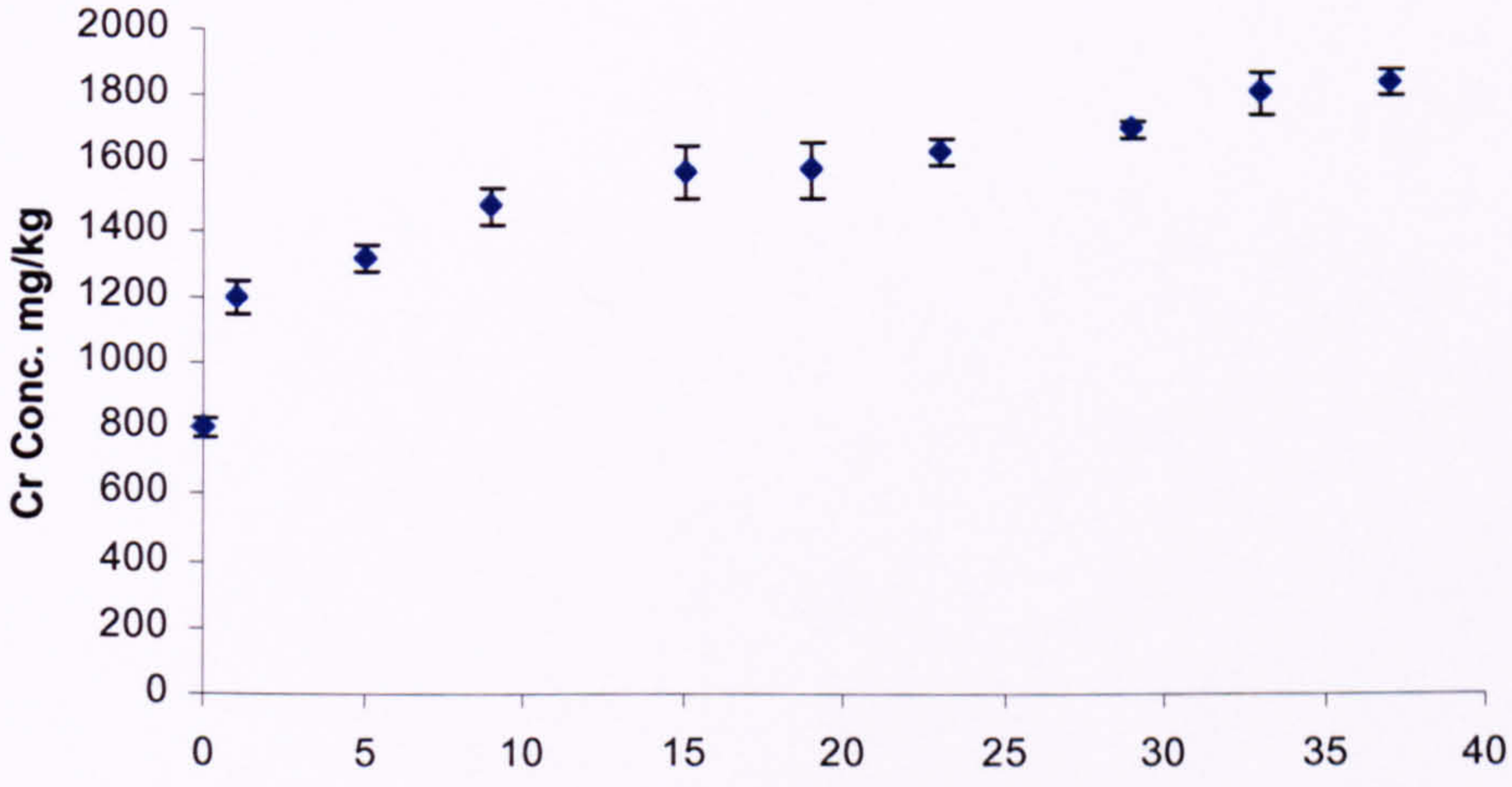


Figure 5-3 Cumulative chromium release with time of shaking (error bars ± 1 STDEV)

The amount of chromium release occurred rapidly at first, with about 66 % of extractable chromium released in the first 24h. Thereafter the chromium release was slower, with three stages being identified (0 – 1 d, 1 - 9 d and 9 - 37 d). This aspect is further discussed and compared with the leach system in Section (5.5.3).

This system was run for 37 days, by which time the chromium released had slowed to 12 mg/kg/d. We do not know if all of the potentially extractable chromium had been released but under this system any further release of chromium would occur at a relatively slow release. The pH was determined each time of soil suspensions and was in the range of 7.3 – 7.5.

The pattern of chromium release from this soil was indicative of dissolution of a small amount of highly soluble chromium - bearing phase, with the bulk of chromium released at a slower rate, presumably from the less soluble source. Deakin et al. (2001) used batch experiments with varying contact times and varying liquid solid (L/S) ratios, carried out on 5 COPR samples taken from a site in NW England. A significant amount of chromium was present (600 - 16300 mg/kg, determined by X-ray fluorescence), but only a small proportion was released by the batch test carried out (0.004 - 1.7 % of the total). However, batch test indicted that chromium was present in at least two forms within the chromite ore processing residue, including a highly soluble and readily leached form and a predominantly insoluble form (primary and altered chromites identified by Energy Dispersive X-ray analysis). Overall, this defined the idea that some of the chromium comes out of soil quickly, but by 4 days the chromium concentration released remains constant, this agrees with the pattern in Figure (5.3), which is some chromium comes out much more slowly when measured on a batch basis (Deakin et al., 2001).

5.5.2. *Column water leaching*

Three columns were used for the column leach experiment. Although the amounts of chromium leached from the columns were different, the pattern of leaching was the same from all three columns. The values obtained from column A are used for detailed discussion below.

Figure (5.4) shows the chromium concentration in solution and (5.5) shows the cumulative soluble chromium released with the volume of solution added to the three columns. The pattern of release was identical, although the concentrations in each column were slightly different, due to the heterogeneous nature of the soil as mentioned previous in Chapter 3, and different due to column packing.

Chromium concentrations were determined in each 100 ml sample of leachate collected, Figure (5.4) reports mean concentration for each 500 ml leached per day. The first 500 ml of solution leached from column A had a mean chromium concentration of 22 mg/l, but this decreased over a 2 months period, after leaching with 10 litres of water, to a concentration 2.5 mg/l.

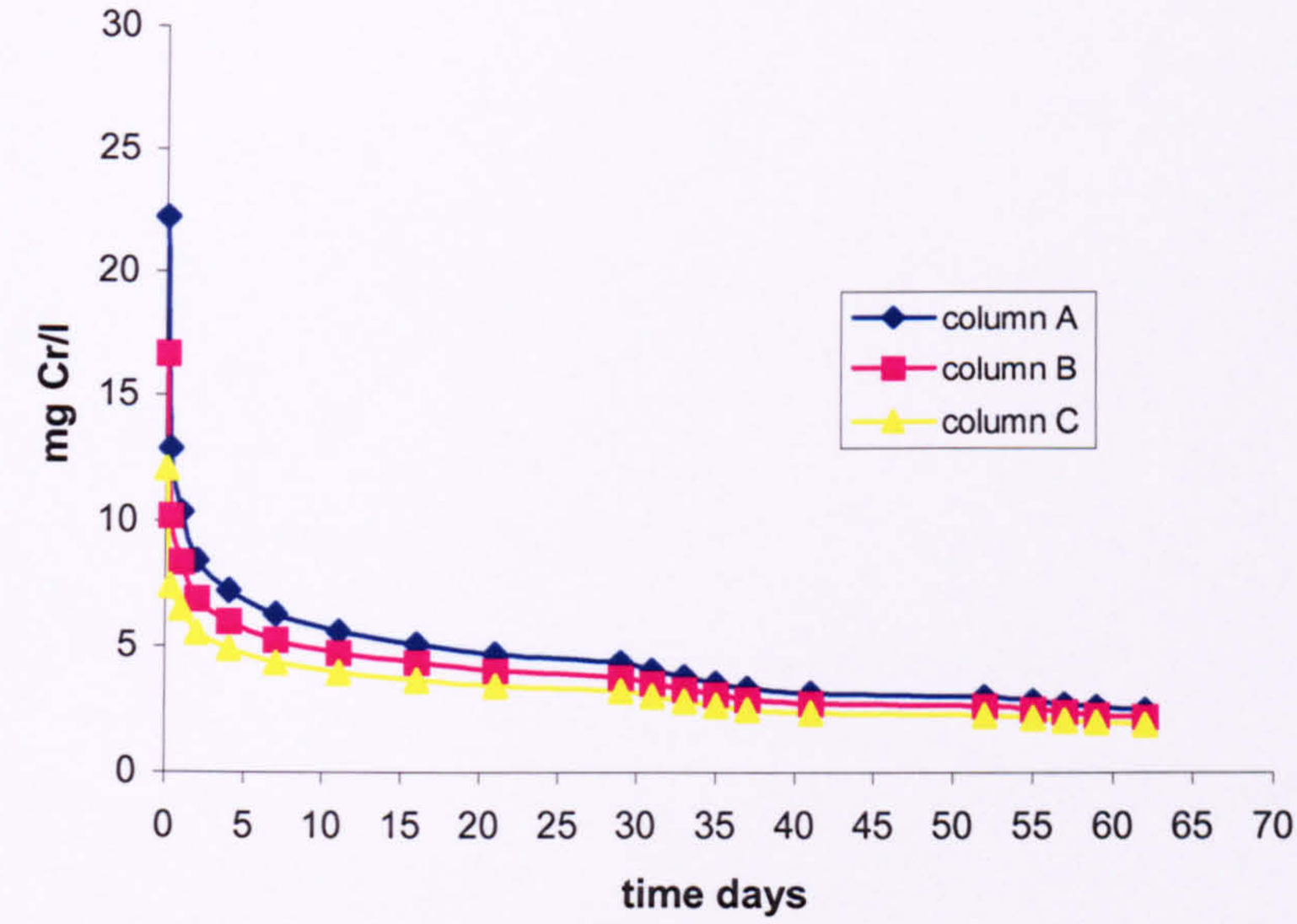


Figure 5-4 Chromium concentration in column leaching with the time factor

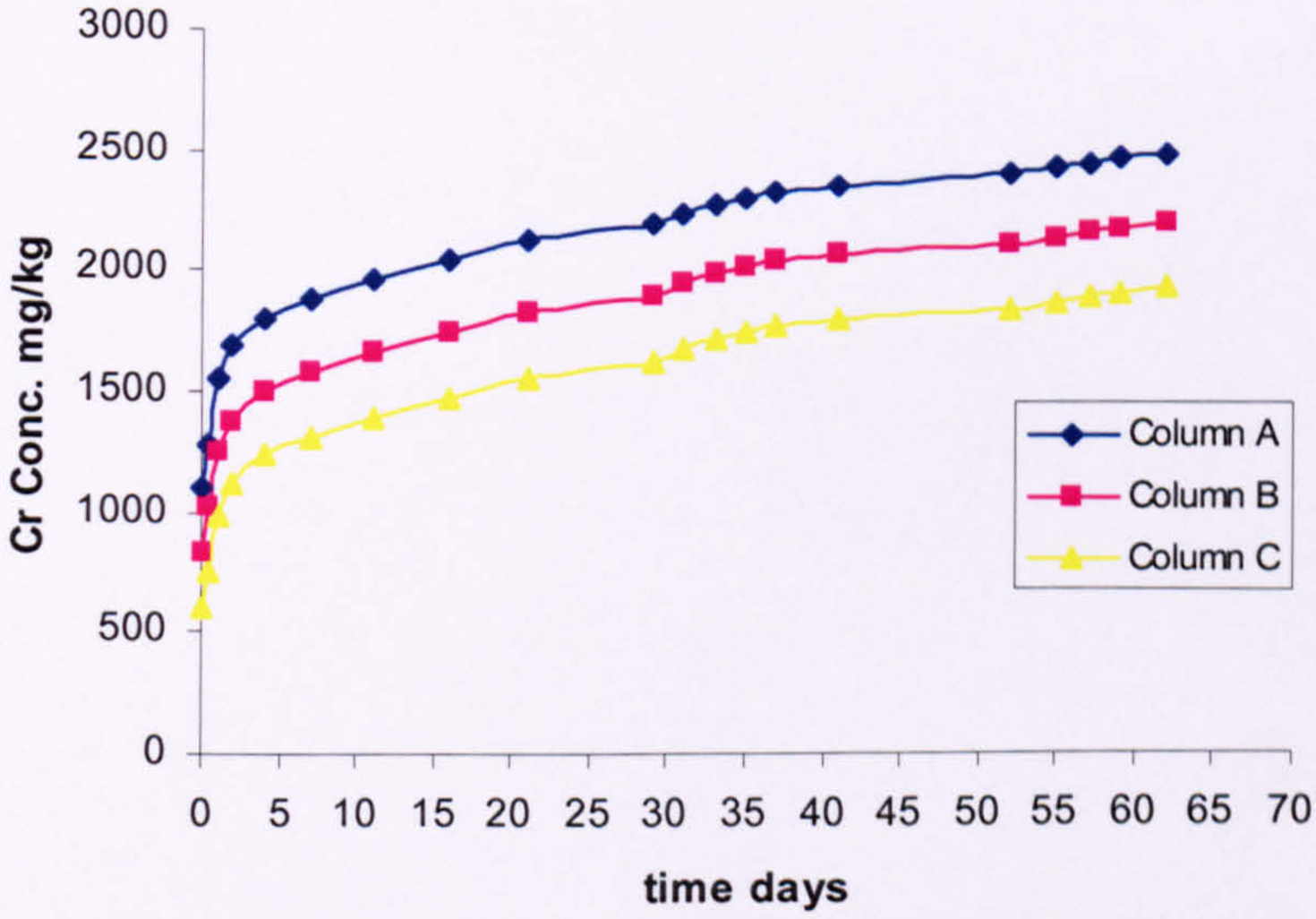


Figure 5-5 Cumulative chromium released with time and the cumulative volume

The cumulative amount of chromium released as leaching progressed is illustrated in Figure 5.5. Initial leaching released around 10 mg chromium from 10 g soil, which equates to approximately 1000 mg Cr/kg, agreeing very well with mean value of samples 9 and 10 reported in Chapter 3. This also agrees with the approximately 800 mg Cr/kg measured after 1h in the batch system in Section (5.5.1).

Thereafter in the leaching system, the amount of chromium released more than doubled by continuing leaching over 60 days, to about 25 mg Cr (equating to 2500 mg Cr/kg). However, this is only about a third of the mean of samples 9 and 10 of total amount of chromium by aqua regia digestion (7300 mg Cr/kg samples 9, 10 see Section 3.5).

In the leaching experiment there was an initial fast release of chromium (1-11d), followed by a slower release (11-37d), conforming to what was found in the batch system. This aspect is further discussed and compared with the batch system in Section (5.5.3). After leaching with 10 litres the mean concentration was around 2.5 mg Cr/l, so it would seem probable that chromium would continue to leach at a concentration of around 1 - 2 mg Cr/l. That is above the environmental quality standard for dissolved chromium on ground water, which is 5 - 50 µg/l depending on the hardness of the solution (Geelhoed et al., 2001).

In fact, a few percent (0.04 %) of total chromium in COPR waste material is released in the readily leachable hexavalent form as known earlier from Chapter 3 for the soil samples 9 and 10. However, there is more chromium, which does not leach immediately, but leaches slowly over time. This does not mean that chromium leaching was complete in this experiment, but any further release of chromium will be relatively slow (Figure 5.5). Thus, there is a concern that groundwater may become contaminated from leaching of chromium from overlying waste.

Farmer et al. (2002) measured concentrations of 7.4 - 125 mg/l in the pore water of soils containing high total chromium concentrations at 3 - 11 m depth adjacent to the chromium dumpsite in Glasgow, using inductively coupled plasma-optical emission spectromctry (ICP-OES) and speciated isotope dilution mass spectrometry (SIDMS) methods. The chromium was predominantly (64-98%) in the form of Cr (VI). The chromium concentration in ground water at the dumpsite was 6.55 - 15.2 mg/l, and concentrations decreased to 0.11 mg/l in the River Clyde (Farmer et al., 2002).There is evidence that chromium has been leached from the contaminant land to the ground water and River Clyde. Further studies in Italy and Poland have confirmed the field observation that hexavalent chromium is readily leachable from chromite ore processing residue (COPR) waste material sites and may result in groundwater concentrations that exceed groundwater quality criteria (Facchinelli et al., 2001; Stpniewska and Bucior, 2001).

When looked at more carefully by considering the chromium concentration in each 100 ml portion of leachate, each flushing cycle had a complicated pattern. Three flushing cycles are illustrated in Figure (5.6) as examples to show what happened. Following a period of non-leaching, the chromium concentration in the first 100 ml was high (4 - 5 mg/l). This fell to approximately 1 mg/l in the four subsequent 100 ml leaching. This cycle was repeated each time the column was flushed with water following a period when it was not leached. This means chromium was released either by dissolution or by diffusion out of the solid phase.

Farmer et al., (2005) via scanning electron microscopic-energy dispersive x-ray (SEM-EDX) analysis has shown hydrocalumite ($Ca_4\ Al_2\ (OH)_{12}\ CrO_4.6H_2O$), which belongs to the group of layered double-hydroxide minerals, has an interlayer which is almost completely filled with chromate ions and constitutes on average of 92 % of chromium mineral in COPR from the Glasgow sites . This is might explain what happened in Figure

5.6. When the moist soil was left in the column without flushing, chromate ions diffused out of the interlayer space, so that the concentration in the subsequent initial leaching was high.

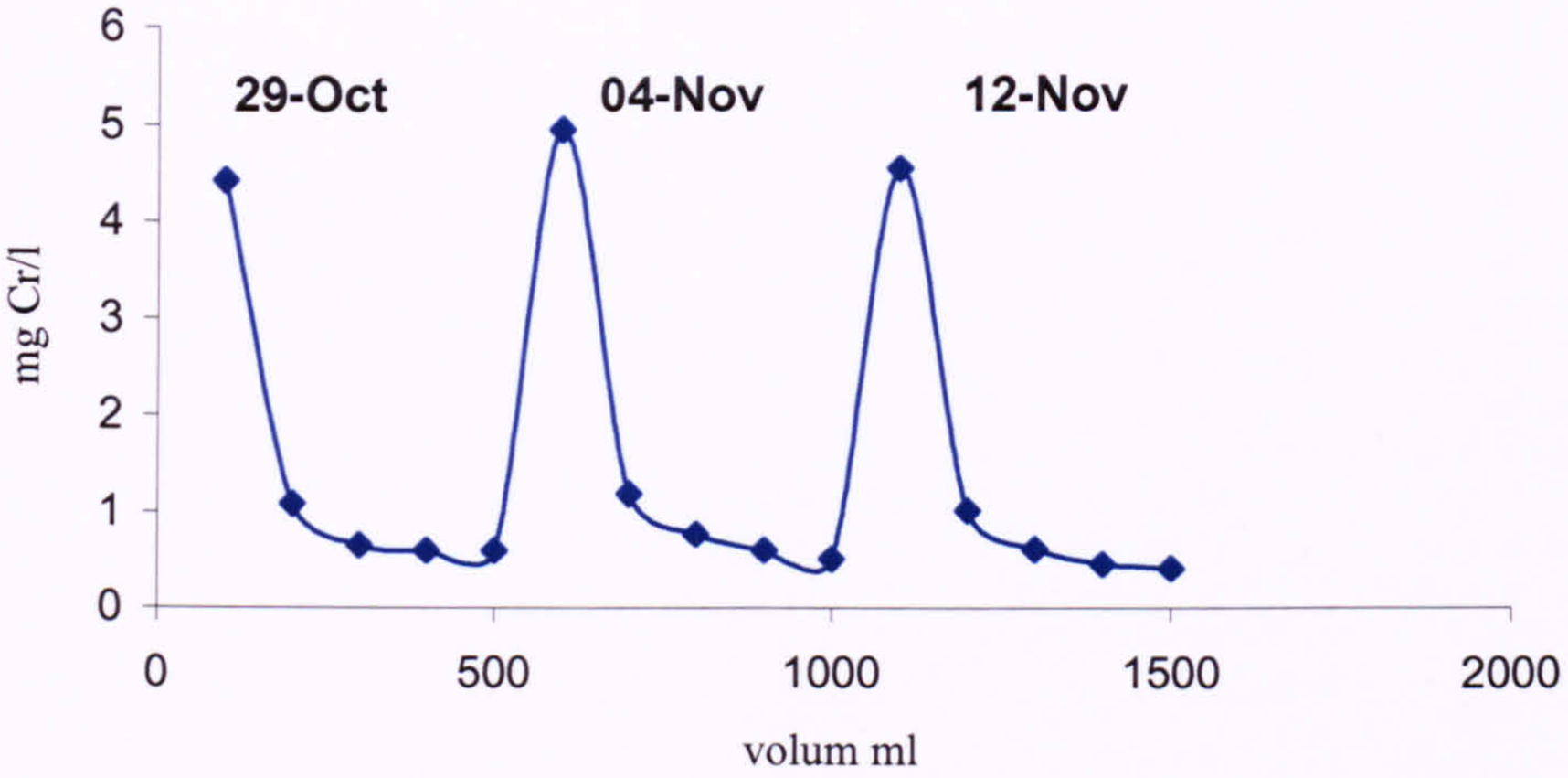


Figure 5-6 Flush of chromium released at the start of each leaching time.

5.5.3. ***Comparison the batch and column systems***

The two sets of results modelled from batch and column studies are very similar and are therefore discussed together as comparison (Table 5.1). The overall amount of chromium leached from soil was approximately the same in batch and column systems 1840 – 2050 mg Cr/kg after 37 days respectively. From Figure 5.3 and 5.5 it is possible to split both the batch and column systems in to 3 stages. For the batch system, the amount of Cr release after 1 day was 1200 mg Cr/g/d, whereas for the column system it was 1260 mg Cr/kg/d. In stage 2 the chromium released was approximately 38 mg Cr/kg/d in batch system and 41 mg/kg/d leached from column system. In stage 3, this value fell to approximately 12 mg Cr/kg/d in batch system and 14 in column system. In the column system, chromium is completely removed from the soil and the soil is continually extracted by fresh water, whereas in the enclosed batch system an equilibrium is established between solid and

solution phases. Nevertheless, that behaviour of chromium release from soil was similar by the two systems. Deakin et al. (2001) and Farmer et al. (2002) used both batch and column systems and found a similar pattern of release of chromium.

This similarity in behaviour could give a concept of chromium release from soil in the field, which could suggest that different remediation methods are required. Reduction methods discussed in Chapter 4 may be suitable for treatment of high concentration of chromium, while adsorption methods may be more appropriate for dealing with the slow, long-term release of chromium. Potential adsorption systems are considered in the next chapter.

Table 5-1 Comparison the amount of chromium released into batch and leach systems in 37 days.

Batch system			**Leaching system**		
Cr released after 37 days 0.92 mg /0.5 g soil		Cr released 1840 mg Cr/kg	Cr released after 37 days 20.5 mg/ 10 g soil		Cr released 2050 mg Cr/kg
Over 37 days split graph in to 3 stages			Over 37 days split graph in to 3 stages		
Stage 1 (0 - 1d)	1200 mg/kg	1200 mg Cr/kg/d	Stage 1 (0 - 1 d)	1262 mg/kg	1260 mg Cr/kg/d
Stage 2 (1 - 9 d)	300 mg/kg	38 mg Cr/kg/d	Stage 2 (1 - 11 d)	413 mg/kg	41 mg Cr/kg/d
Stage 3 (9 - 37 d)	340 mg/kg	12 mg Cr/kg/d	Stage 3 (11 - 37 d)	375 mg/kg	14 mg Cr/kg/d
Total Cr release	1840 mg/kg			2050 mg/kg	

mg Cr/g/d = mg of Cr in 1 g soil per day.

Chapter 6

Remediation of Chromium Contamination by Adsorption

6.1 The design of clean up strategy

The information given in the previous chapter should benefit on-going efforts of workers to remediate chromium-contaminated sites. As the contaminated sites are sometimes located in residential areas, the release of contaminants is of great concern. Therefore a system that results in stabilising or remediating the contaminated sites to minimise chromium release is desirable. Ultimately Figure (6.1) shows the system of the clean up strategy by selecting various materials as a bed of treatment. In this case there is a need to channel the leachate contaminated with chromium through a treatment bed, which is likely to produce clean water from the other side.

To get to this point we need to study different sorbant materials, such as natural charcoal, wood bark, coir, and peat, in batch and column experiments designed to investigate the adsorption-desorption properties of both cationic Cr (III) and anionic Cr (VI). The work described in this chapter will develop this method in more detail.

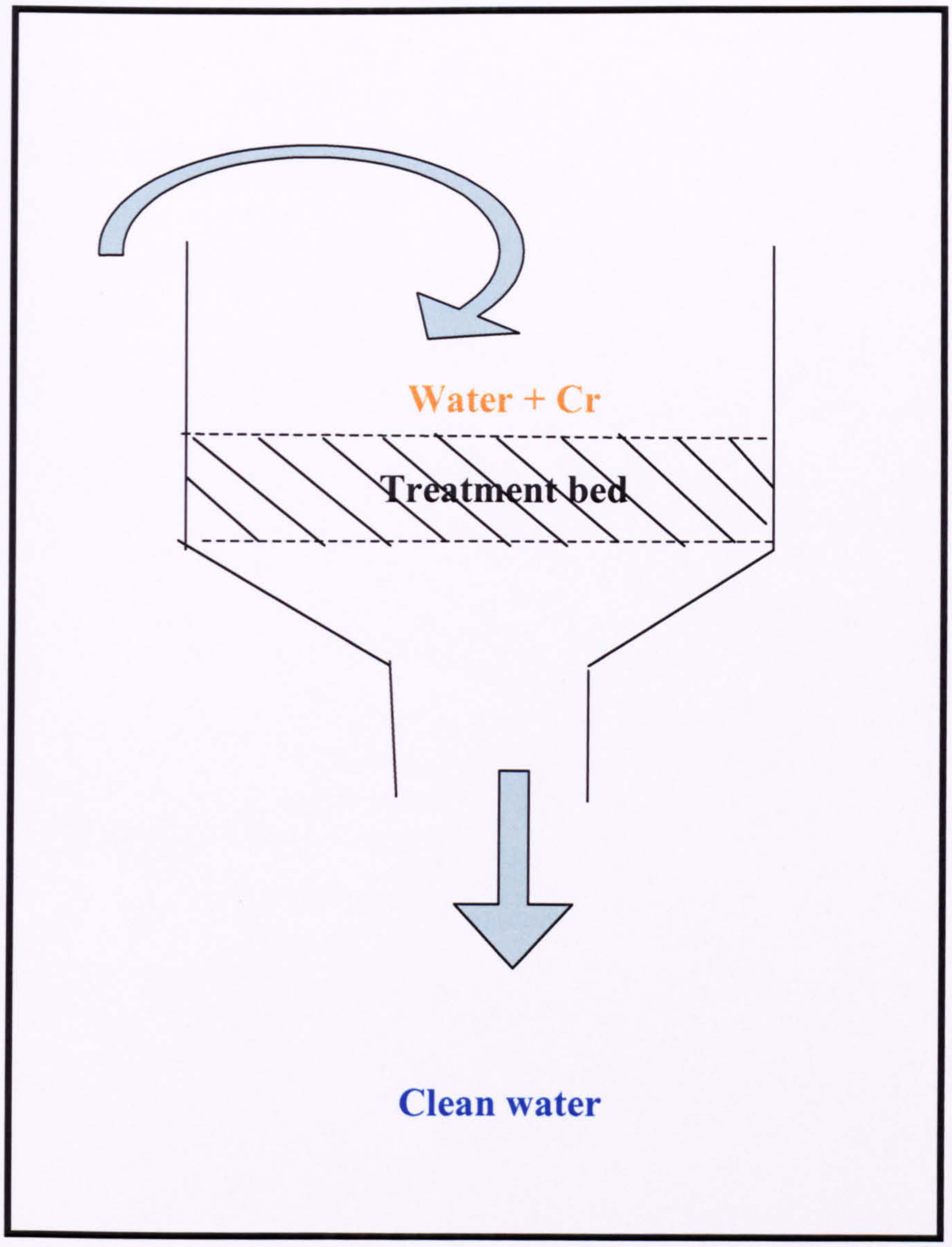


Figure 6-1 The design of the clean up strategy

6.2 Adsorption of Cr (III) and Cr (VI) by different sorbents

6.2.1 Single point experiment

A single point experiment was used to study the sorption characteristics and release of chromium on to different sorbents such as bone charcoal, peat, coir and wood bark. The basis for choosing these sorbents is that they are relatively cheap and available, and also they have previously been used to treat different metals such as Pb, Zn, As, Cd, Cu and Cr (Aggarwal et al., 1999; AlAsheh and Duvnjak, 1997; Dakiky et al., 2002; Vennilamani et al., 2005).

6.2.2 *Materials*

Bone charcoal is known as the product of the dry distillation of animal bones (bone obtained from animals that have died naturally). The bones are normally obtained from India or Pakistan, and are supplied to Brimac Carbon Services in a crushed state. A hopper was used to allow mixed bones of various origin and particle size distribution to be carbonised. The bone is heated in the retorts for a period of 12 hours at varying temperature profiles (from 600 ^{0}C to 1000 ^{0}C). The bone charcoal before being discharged from the retorts was passed through water-jacketed coolers. Thereafter, the charcoal passes over several electro-magnets to ensure the absence of trapped metals, undergoes crushing, particle size grading and screening before final sorting for specific applications.

The manufacturer Brimac Carbon supplied various mesh sizes but the mesh size that used here was uniform and maintained between 20 - 60 mesh. The pH of newly manufactured

bone charcoal is quite alkaline. Brimac Carbon services wash the charcoal with deionised water until the pH of the effluent is < pH 8.

Chempak coir compost, is produced entirely from waste coconut fibres and husks and is, therefore, from 100 % renewable source (it grows on trees) and has been used as a growing medium for many years in Sri Lanka. Coir is supplied as highly compressed blocks, about house brick size, which when moistened will swell to about eight times original size to produce loose coir. The coir was then spread on to a plastic sheet at the lab to dry at room temperature over two days, and then ground to about size range of 1.5 - 4 mm and stored in plastic bags until use. The coir organic matter percentage was ≥ 93 % and coir pH was 5.6.

Humax Garden Peat is produce by a unique process combining the upper sphagnum layer with the deep sedge – type layer in peat deposits. The peat organic matter percentage was ≥ 95 % and the peat pH =3.9.

Wood bark, a fine grade bark, comes from Spruce and Pine trees and is harvested in the north of Scotland. The bark is processed up to 4 months before despatch and supplied by ScotBark. 10 g of wood bark mixed with 30 ml deionised water had a pH = 5. The organic matter percentage at wood bark was > 90 %. The individual particles of wood bark range up to approximately 3-5 cm in length

6.2.3 *Method of batch experiment*

This method is similar to that outlined in Chapter 2 (Section 2.9.). Approximately 1g of each sorbant was weighed into a bottle (all sorbents were used as received, except coir which was treated as above mentioned). 50 ml of initial chromium concentration of 50 mg/l was added in triplicate then shaken for 60 min. Then 47 ml of solution was decanted

and filtered through Whatman No.2 filter paper and the resulting filtrate collected in plastic bottles for storage until analysis. For desorption, 50 ml of deionised water was added to the 3 ml remaining and the slurry again shaken for 60 min. After that the slurry was filtered. The equilibrium concentration value of the filtrate solution measured on the AAS was then used to calculate the amount of chromium adsorbed and desorbed per g of sorbents described in Chapter 2 (Section 2.9.2.2).

6.2.4 Results and Discussion

Figure (6.2) shows that Cr (III) was removed from the solution by all four sorbents, with about 77 % on wood bark, 86 % on peat, 96% on coir, and 100% on bone charcoal of the added chromium being adsorbed. In terms of desorption, no Cr (III) was returned back to the solution following desorption from all sorbents.

Figure (6.3) shows that 38% and 40% of the Cr (VI) added adsorbed on to wood bark and peat respectively. The Cr (VI) was held firmly on to wood bark and peat and did not desorbs there may even have been slightly more adsorption. Bone charcoal was the poorest adsorber, with about 7 %, and coir 26 % of the Cr (VI) removed from the solution. Some of this chromium returned back to the solution following desorption so on all the sorbents more Cr (III) was adsorbed than Cr (VI). Using this single point method it was not possible to judge which amendment could remove chromium from solution so the next experiment was used to study the capacity of each amendment to remove chromium from a wide range of chromium concentrations.

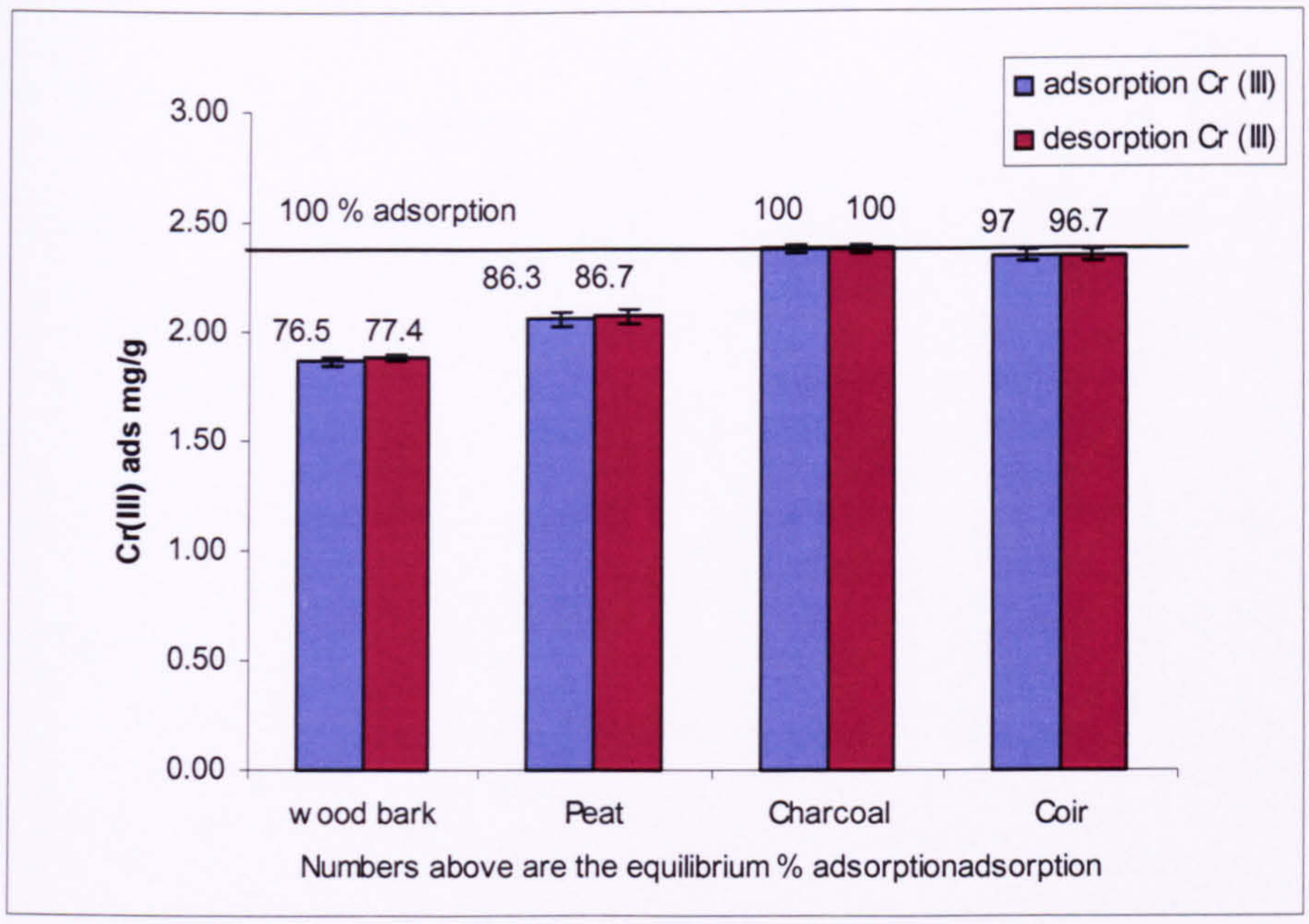


Figure 6-2 Adsorption and Desorption of Cr (III) with different sorbents.
Horizontal line shows 100% adsorption based on initial chromium concentration.
*** There is no significant different between the adsorption and desorption.**

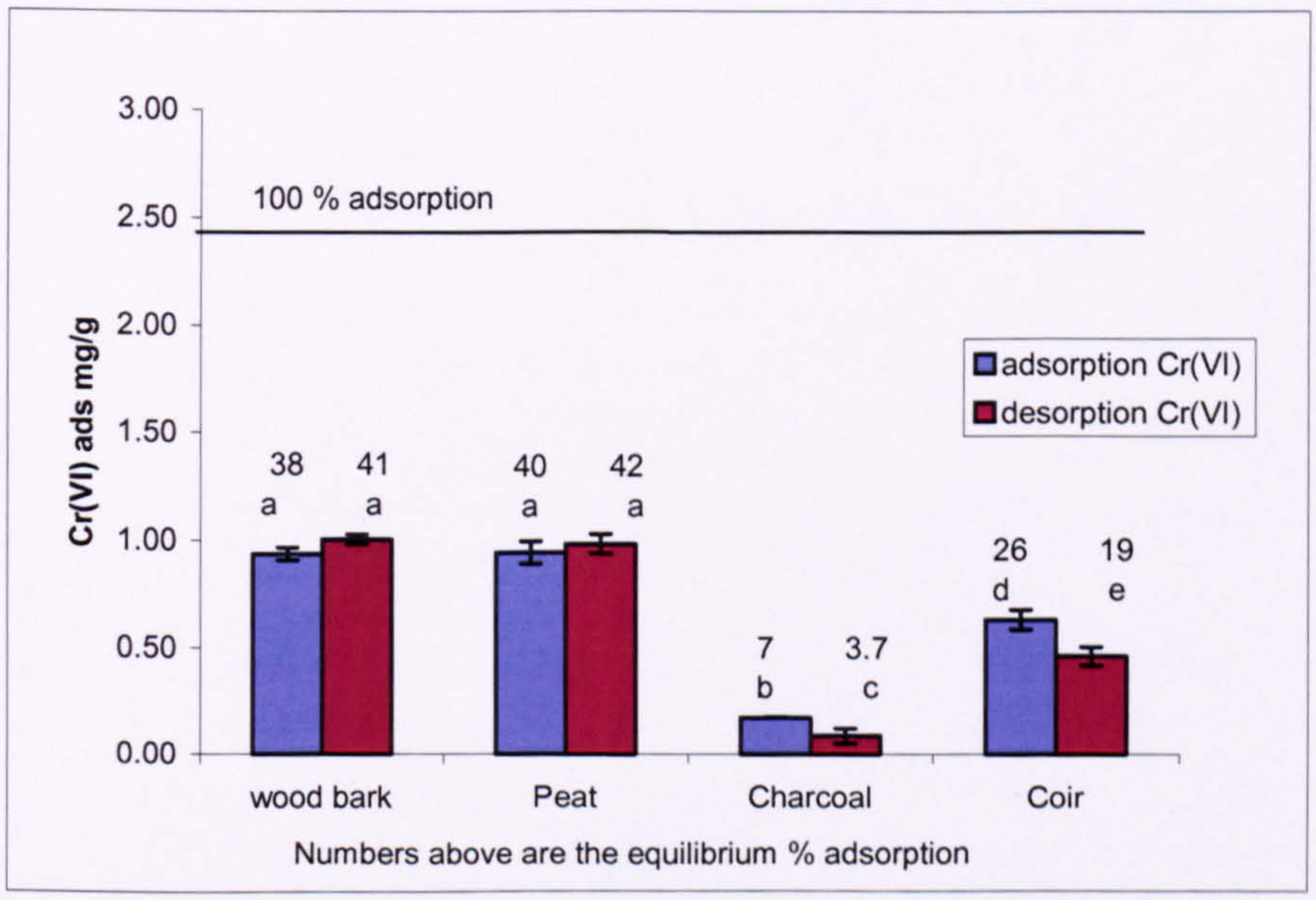


Figure 6-3 Adsorption and Desorption of Cr (VI) with different sorbents.
Horizontal line shows 100% adsorption based on initial chromium concentration.
*** The columns with the same letters are not significantly different and the different letters are significantly different (5% Tukey LSD)**

6.3 The capacity of different sorbents to adsorb chromium from solution

6.3.1 Aim

To assess the extent to which sorbents could remove chromium from wastewater using batch tests.

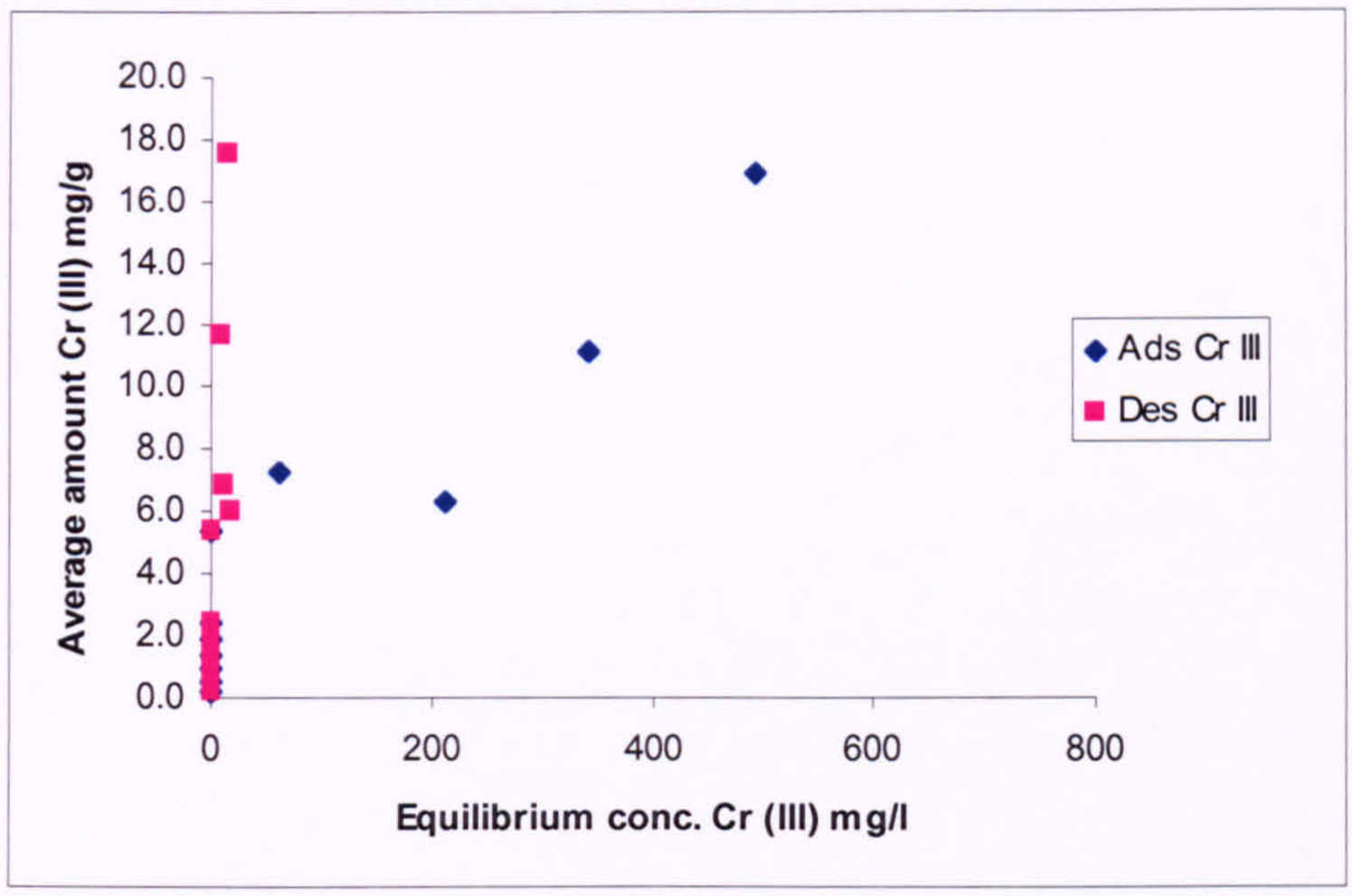
6.3.2 Method

The method established in chapter 2 (see Section 2.9.2) for the batch experiment was used. 1 g of each sorbent (charcoal, wood bark, coir, peat) was weighed, and then 50 ml of chromium solution was added in the concentration range (5, 10, 20, 30, 40, 50, 100, 200, 400, 600 mg/l) for the majority of experiments. In some cases the range was up to 800 mg/l to allow an equilibrium capacity to be obtained. The samples were shaken for 1h as a suitable time for comparison between the four sorbents.

6.3.3 Result and Discussion

Figures 6.4 - 6.10 show the sorption isotherms and Langmuir modelling for each of the sorbents. Figure (6.4) shows that at an initial Cr (III) concentration of 100 mg/l or less, nearly all the Cr was adsorbed on to bone charcoal. Some chromium remained in solution at equilibrium from the initial solutions of > 100 mg Cr/l, but no obvious adsorption maximum was observed. The adsorption isotherm for Cr (VI) on to bone charcoal was convex to the *x* axis and did not show an adsorption maximum. Desorption showed that over 99 % of the Cr (III) applied was held firmly, particularly at low concentration, while

up to 70 % of Cr (VI) was desorbed from the bone charcoal, so Cr (VI) is bound less strongly than Cr (III).



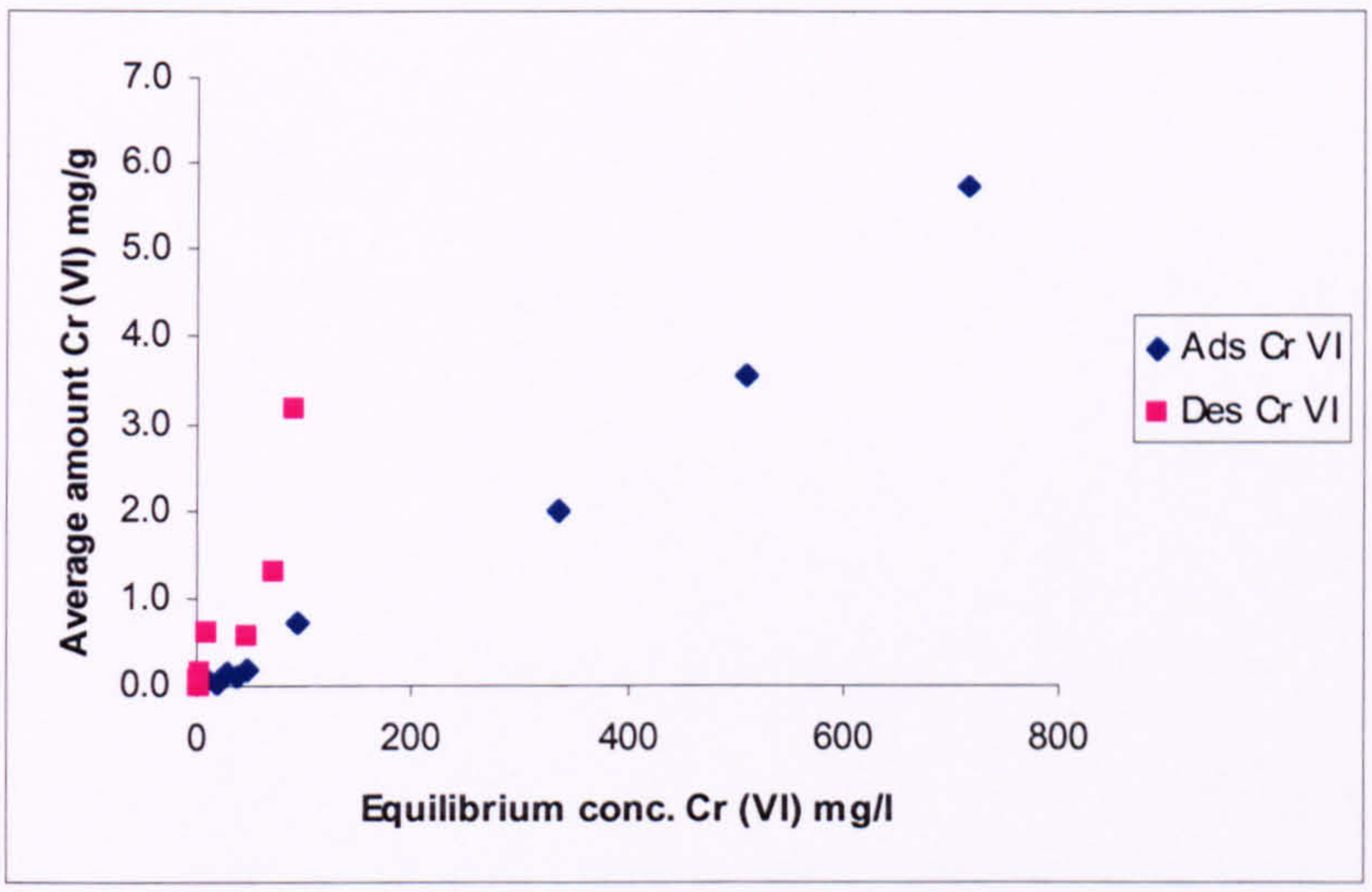
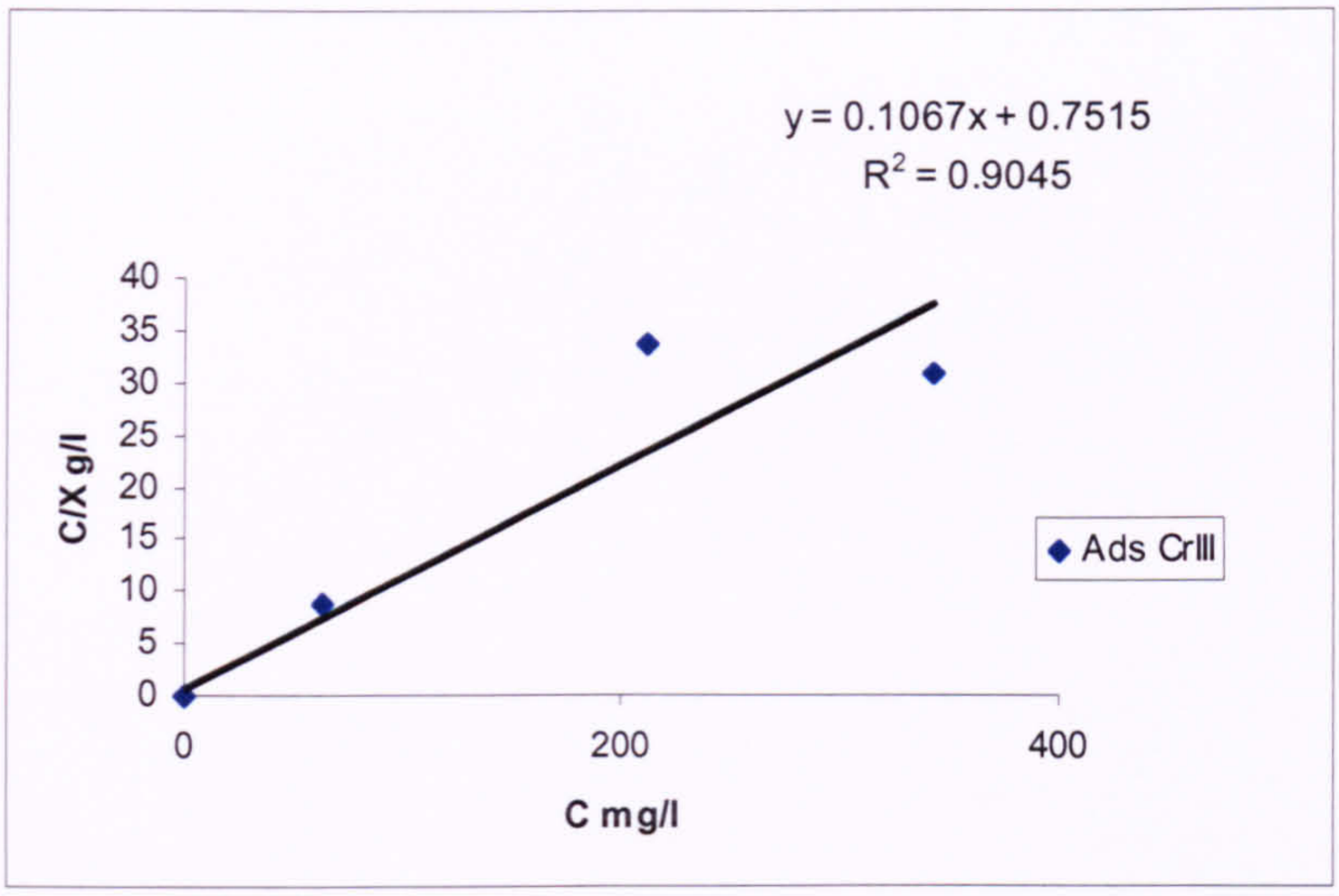


Figure 6-4 Adsorption and Desorption of Cr (III) and Cr (VI) by bone charcoal



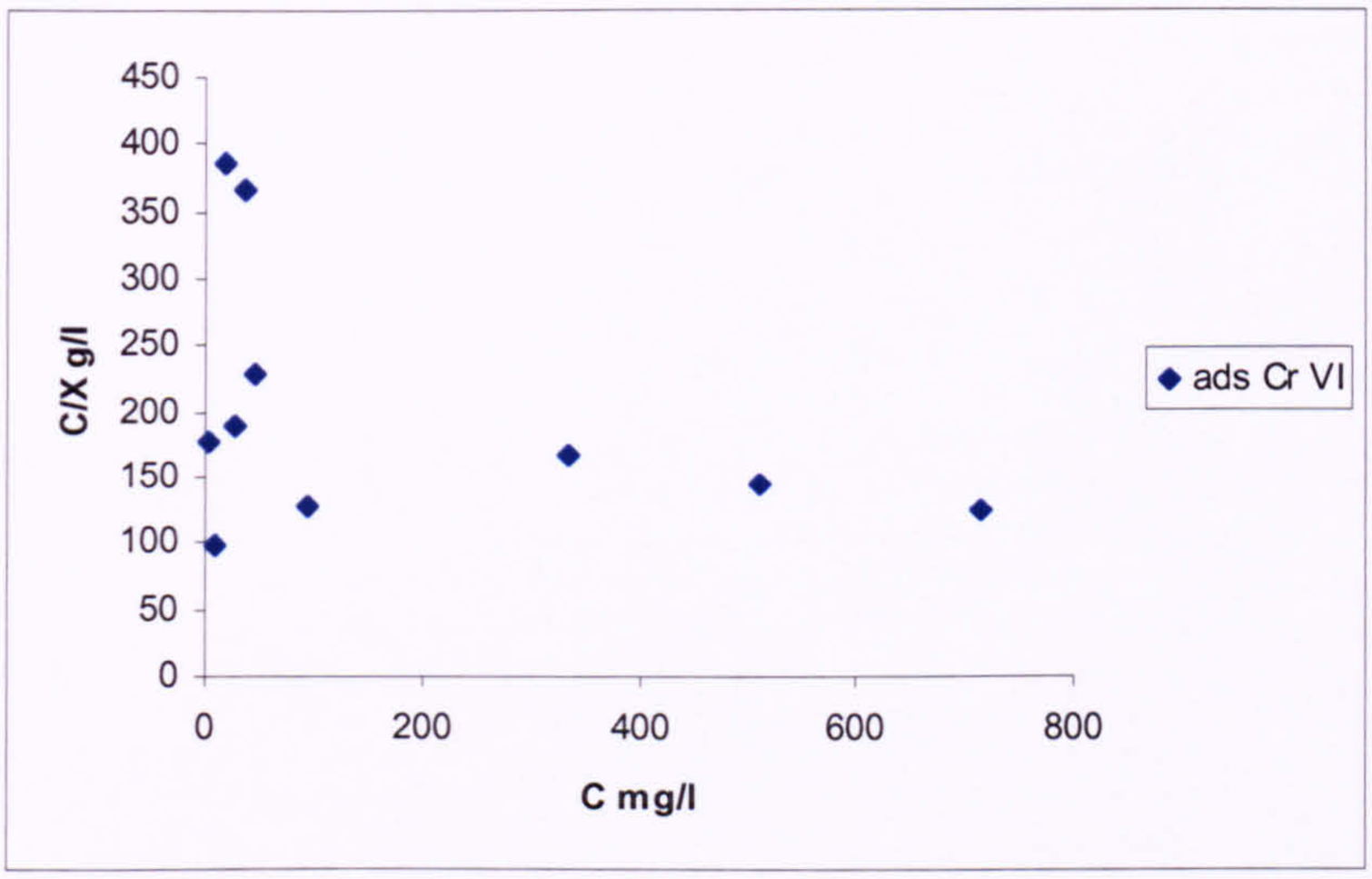
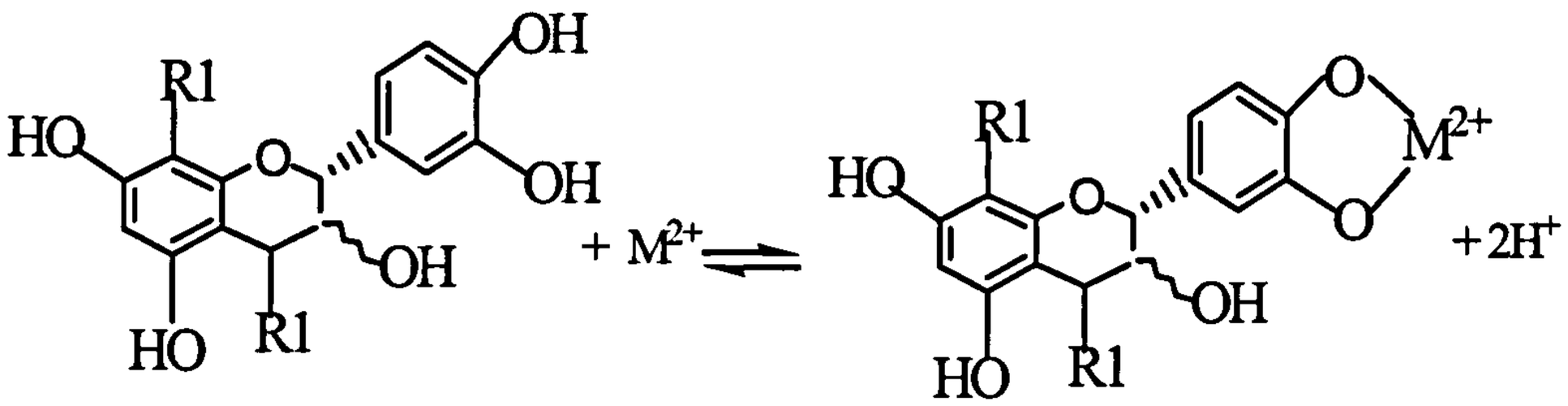


Figure 6-5 Langmuir isotherm of chromium adsorbed on bone charcoal

Figure (6.5) shows the Langmuir equation applied to adsorption of Cr (III) on to bone charcoal, giving X_{max} of 9.37 mg/g Cr (III) adsorbed. Application of the Langmuir isotherm has been used to assess the theoretical maximum binding capacity of cationic metals (Cu, Cd and Zn) by bone charcoal (Cheung et al., 2001a; Ko et al., 2004; Panichev et al., 2003; Wilson et al., 2003) The data for Cr (VI) adsorbed on to bone charcoal did not follow the Langmuir isotherm model, so it was not possible to get the X_{max} capacity of bone charcoal to adsorbed Cr (VI) (Figure 6.5). The highest measured adsorption of Cr (VI) by charcoal was 6 mg/g from an initial concentration of 800 mg/l. The explanation for the phenomena observed for both forms of chromium adsorbed on to bone charcoal could

be as (Abram and Hensel, 1964)_showed the surface charge on bone charcoal when placed in water of pH 7 was negative. Therefore anions will naturally not be attracted to a negative surface. Ligand exchange may still occur and be an important influence. As metal cations are sorbed the influence of anions may become more evident. Wilson et al., (2001) and Wilson (2001) studied the mechanism of chromium adsorption on to bone charcoal and showed that the ratio of chromium sorbed to Ca released was 1:1, based on the charge equivalents of Cr (III). The charge equivalents of Cr (VI) did not balance. This indicated that perhaps Cr (VI) is reduced to Cr (III) before it is sorbed, and so has the same Ca:Cr ration.

Adsorption isotherms of both forms of chromium with wood bark show a rapid initial rise in chromium sorbed at low concentration (Figure 6.6). Desorption of the two forms of chromium is similar. Over 99 % of the Cr (III) applied was held firmly, while more than 10 or 20 % of Cr (VI) added removed back to the solution (Figure 6.8). The data of Cr (III) fitted well when modelled by the Langmuir equation, with R^2 value 0.985 (Figure 6.7). The binding capacity of Cr (III) is X_{max} 5.2 mg/g. The Langmuir adsorption isotherm did not fit the Cr (VI) data and had R^2 value 0.548 (Figure 6.9). Bark has been used for removing metal ions from aqueous solution (Palma et al., 2003). Vazquez et al., (2002) suggested that bark contains polyphenols based on procyanidin and this could act as ion exchange, the deprotonated hydroxyls of the procyanidin ring chelating divalent cations Equation (6.1). The possibility arises in using this byproduct to remove heavy metal cations from wastewater.



Equation 6-1

The non-uniform particle size of wood bark was given a problem of a variability between the replicate and it is clearly at high chromium concentration that might be due to the surface site limitation and this also had fund when studied > 4 mm wood bark on different particles size in (Section 6.6.3). This problem did not arise with peat and coir that because of the uniform particle size lead to have a good replicate.

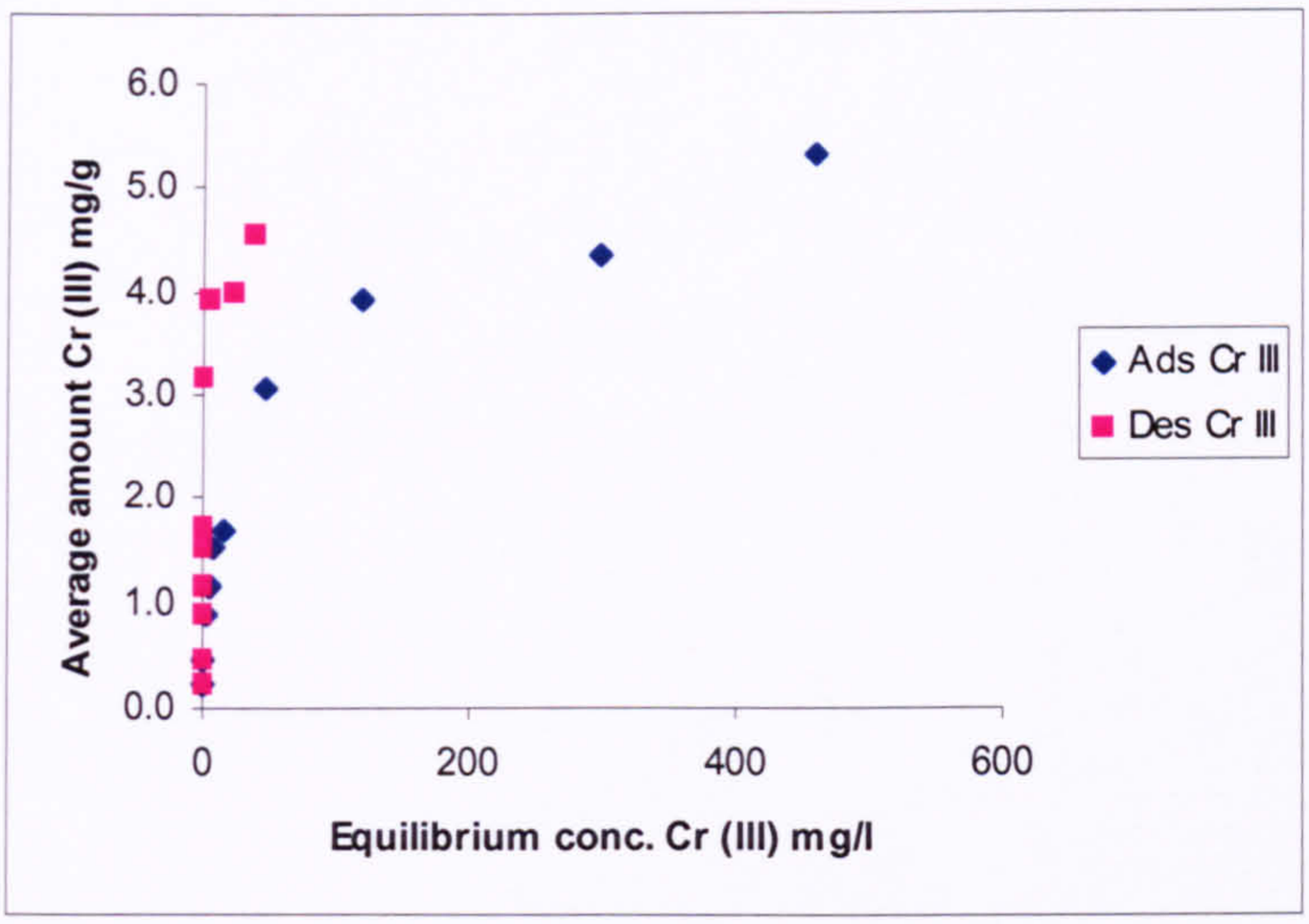


Figure 6-6 Adsorption and Desorption of Cr (III) by wood bark

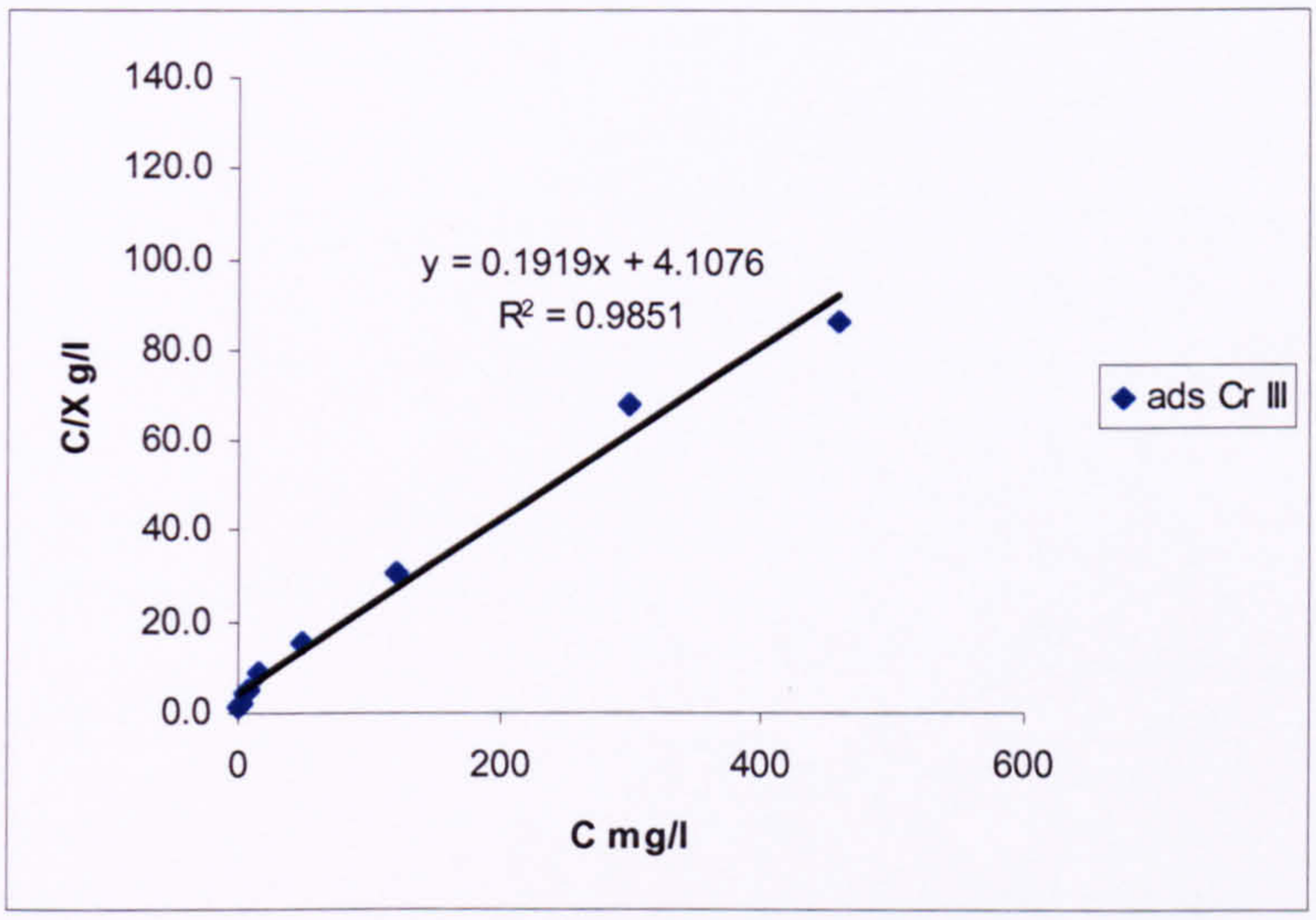
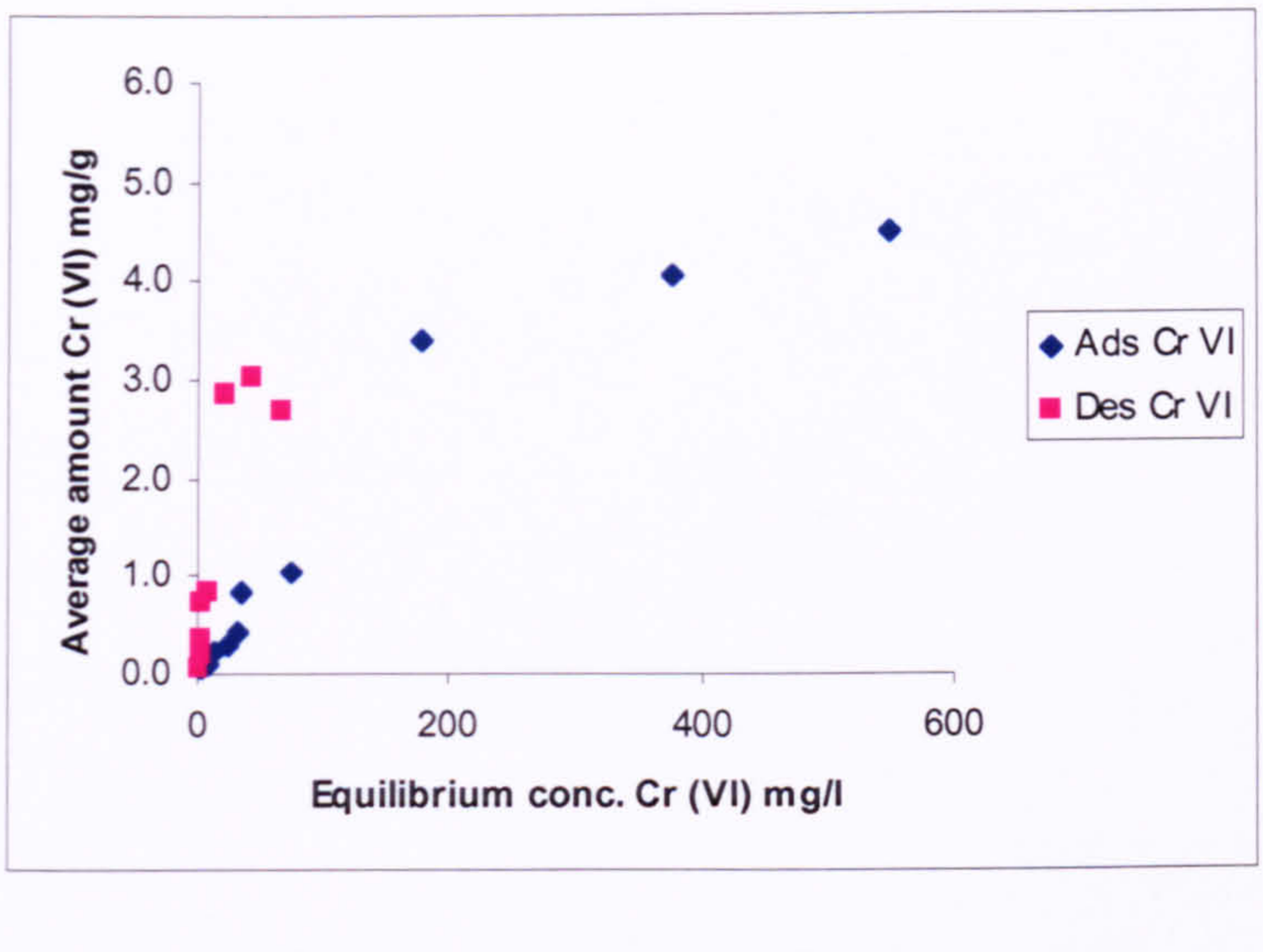


Figure 6-7 Langmuir isotherm of Cr (III) adsorbed on Wood bark



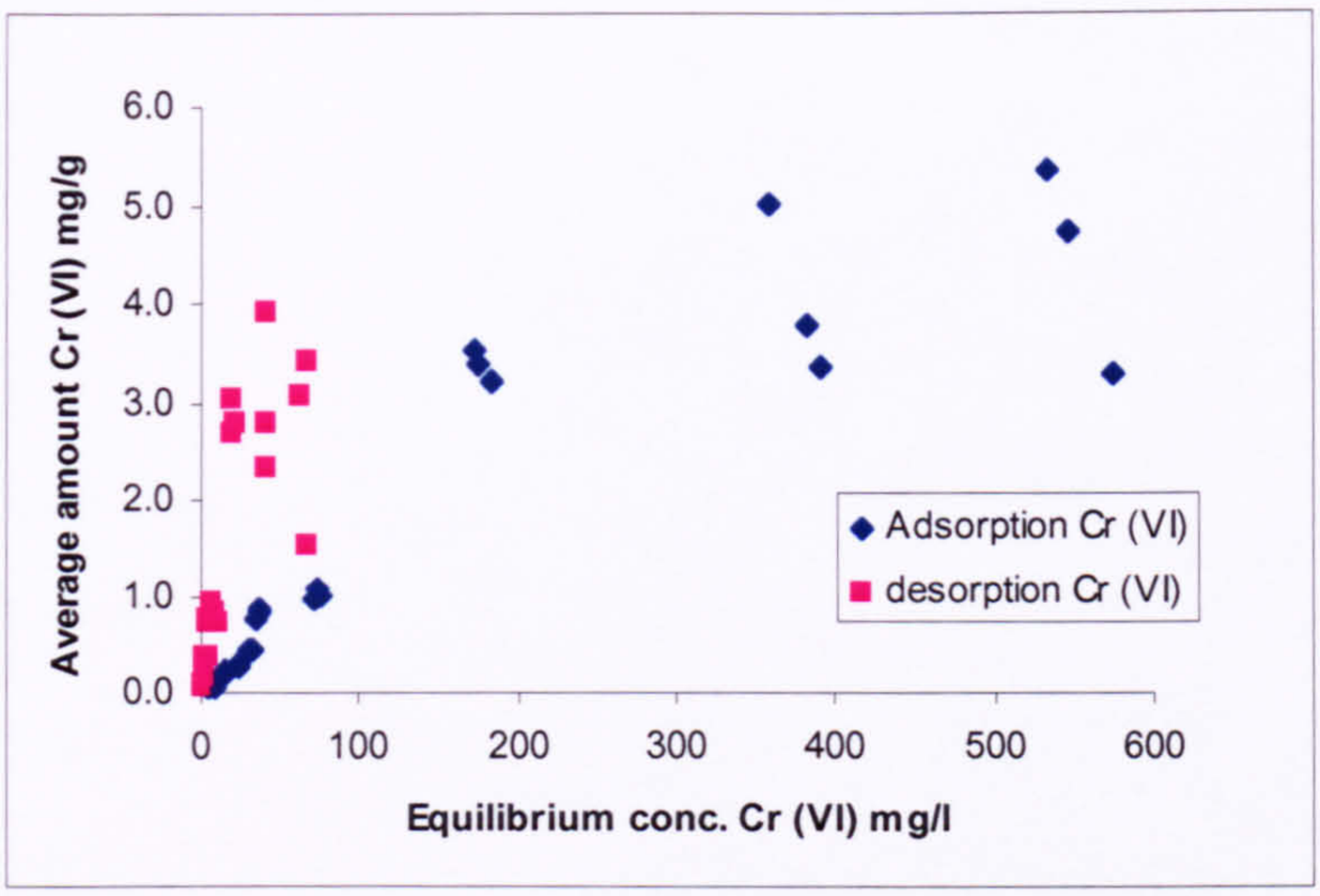


Figure 6-8 Adsorption-Desorption the mean of Cr (VI) and the replicates by wood bark

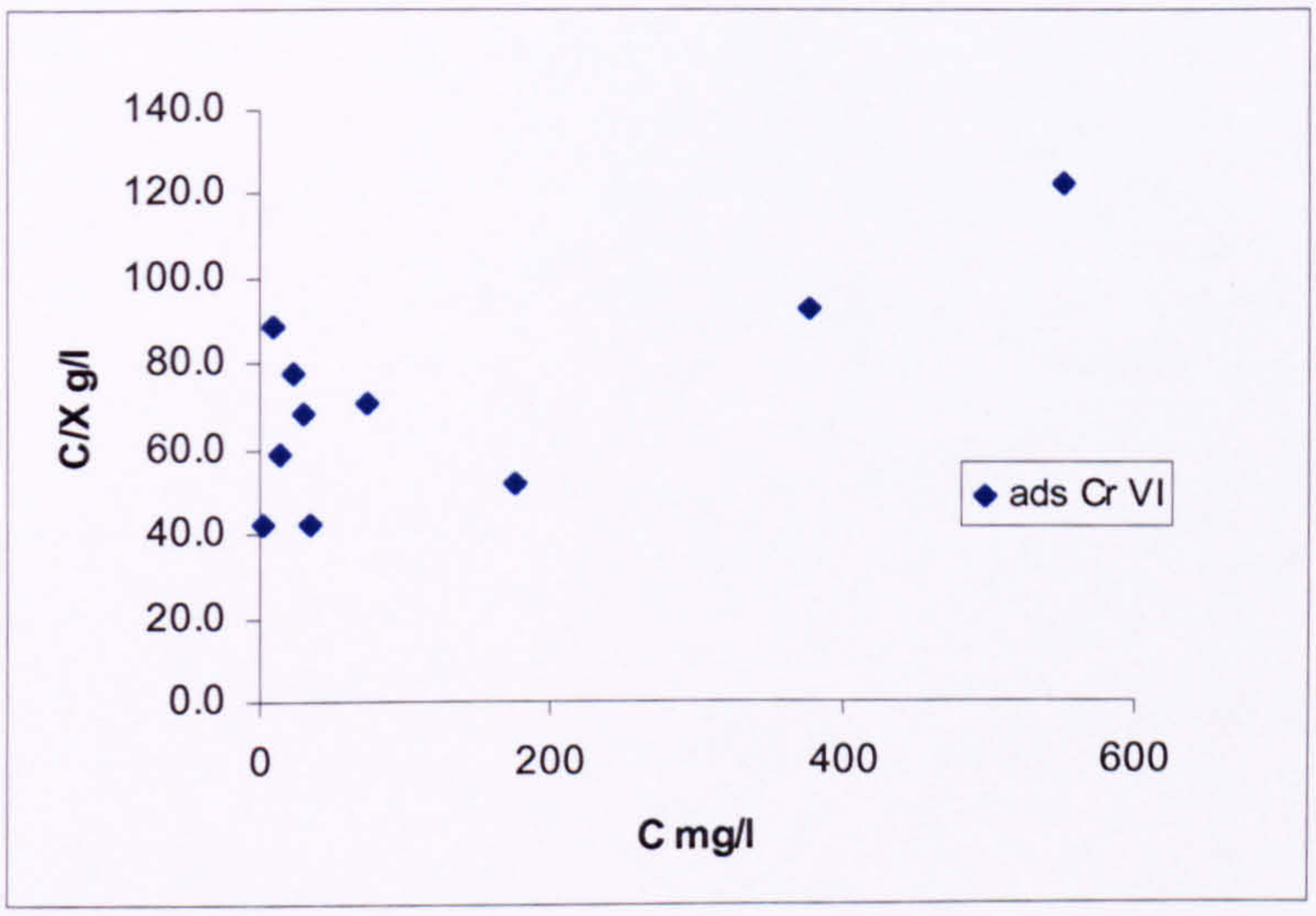


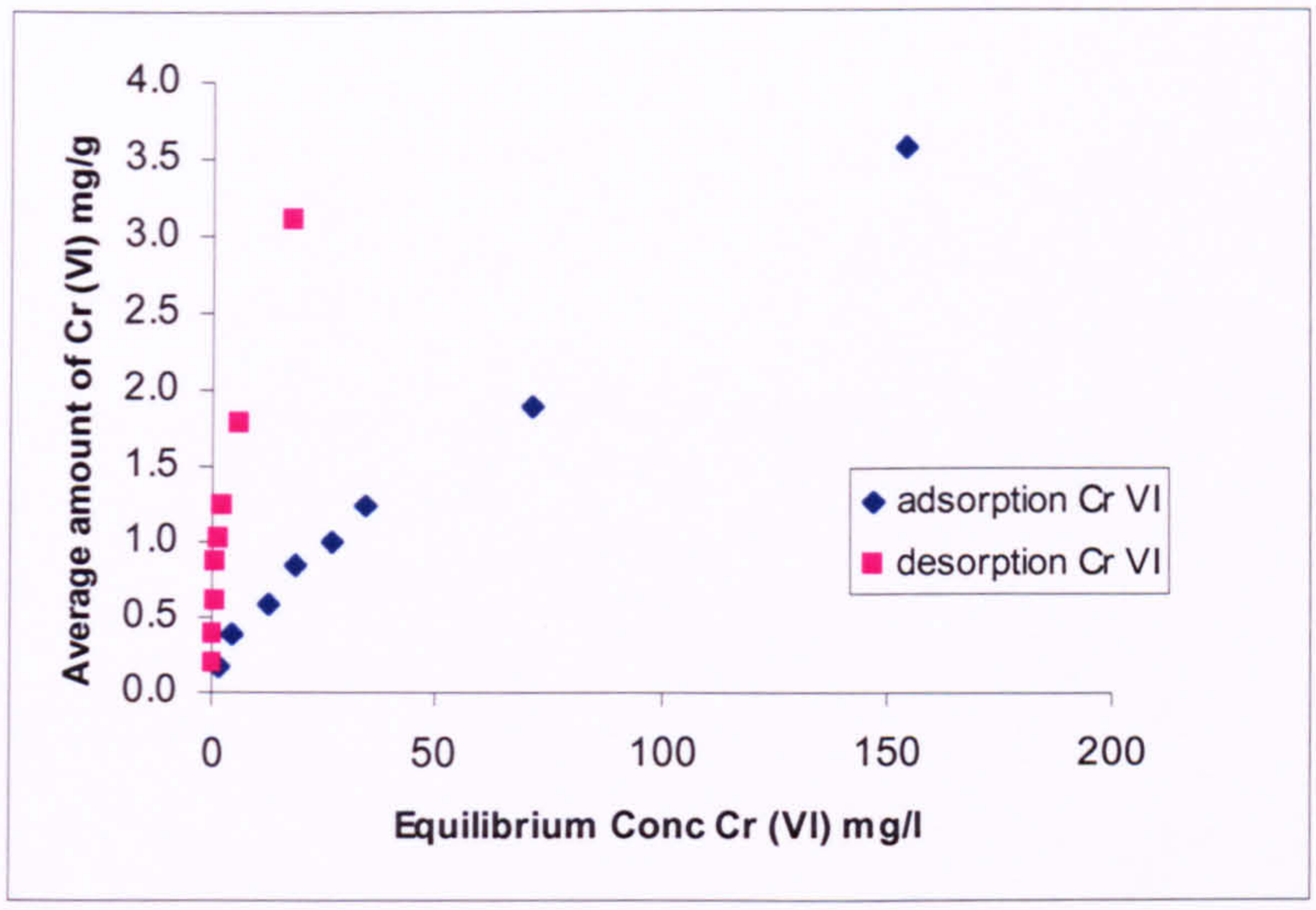
Figure 6-9 Langmuir isotherm of Cr (VI) adsorbed on Wood bark

The adsorption isotherms with peat and coir were done only with Cr (VI), which is the form of concern as mentioned earlier. Figure (6.10) shows that Cr (VI) adsorption on to peat is follow a more typical isotherm than those shown above for bone charcoal and wood bark. These data however do not fit a single straight line when applied to the Langmuir model (Figure 6.11), but two straight lines can be fitted. There has been considerable debate about the splitting of Langmuir isotherm, with, for example, Shuman, (1975) suggesting that the two lines represent surfaces of different bending energies, while Pulford, (1986) thought that the fitting of two lines may be an artifact of the distribution of the data points, which more probably fit a curve. If, however, two lines are fitted as in Figure 6.11, they give an *x* max value of 1.4 mg Cr/g for the low concentration range and 7.7 mg Cr/g for the high concentration range. The desorption isotherm shows that no chromium desorbed at low concentrations, but some Cr (VI) was desorbed at higher concentration. The functional groups present on the surface of peat are mainly carboxylic, hydroxyl, and phenolic groups. The physicochemical interactions that might occur during Cr (VI) removal could be expressed as (Equation 6.2) were (-COOH) represents the surface functional group of peat and *n* is the coefficient of the reaction component, depending on the oxidation state of metal ions, while M^{n+} and H^{+} are Cr (III) and hydrogen ions, respectively (Kurniawan et al., 2006). This assumes that Cr (VI) is reduced to Cr (III) by the organic matter (Park et al., 2006) which is discussed in more detail below.

$$M^{n+} + n\,(\text{-COOH})\,X \quad (\text{-COO})_n\,M + n\,H^{+} \qquad \textbf{Equation 6-2}$$

Figure (6.12) shows sorption isotherm for Cr (VI) with coir, which behaved similarly to peat. The data fitted the two stages Langmuir isotherm with *x* max of 2.3 and 4.1 mg Cr/g over the low and high data points respectively (Figure 6.13). Desorption found that no chromium desorbed at low concentrations but over 20 % at the top point. The coir pith as

low cost adsorbent could be used as an efficient adsorbent material for the removal of Co (II), Cr (III) and Ni (II) from water (Parab et al. 2006).



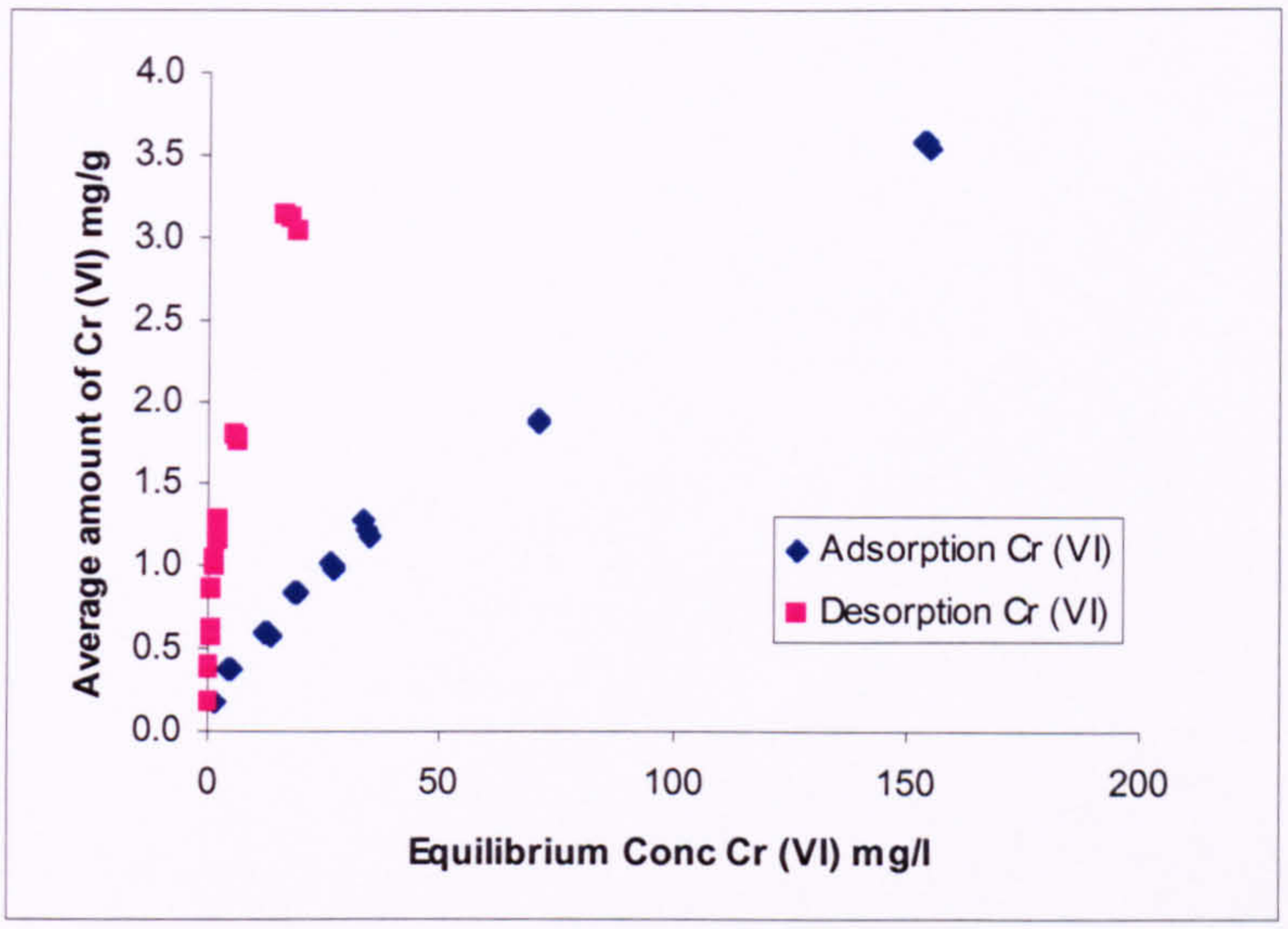


Figure 6-10 Adsorption- desorption the mean of Cr (VI) and the replicate by Peat.

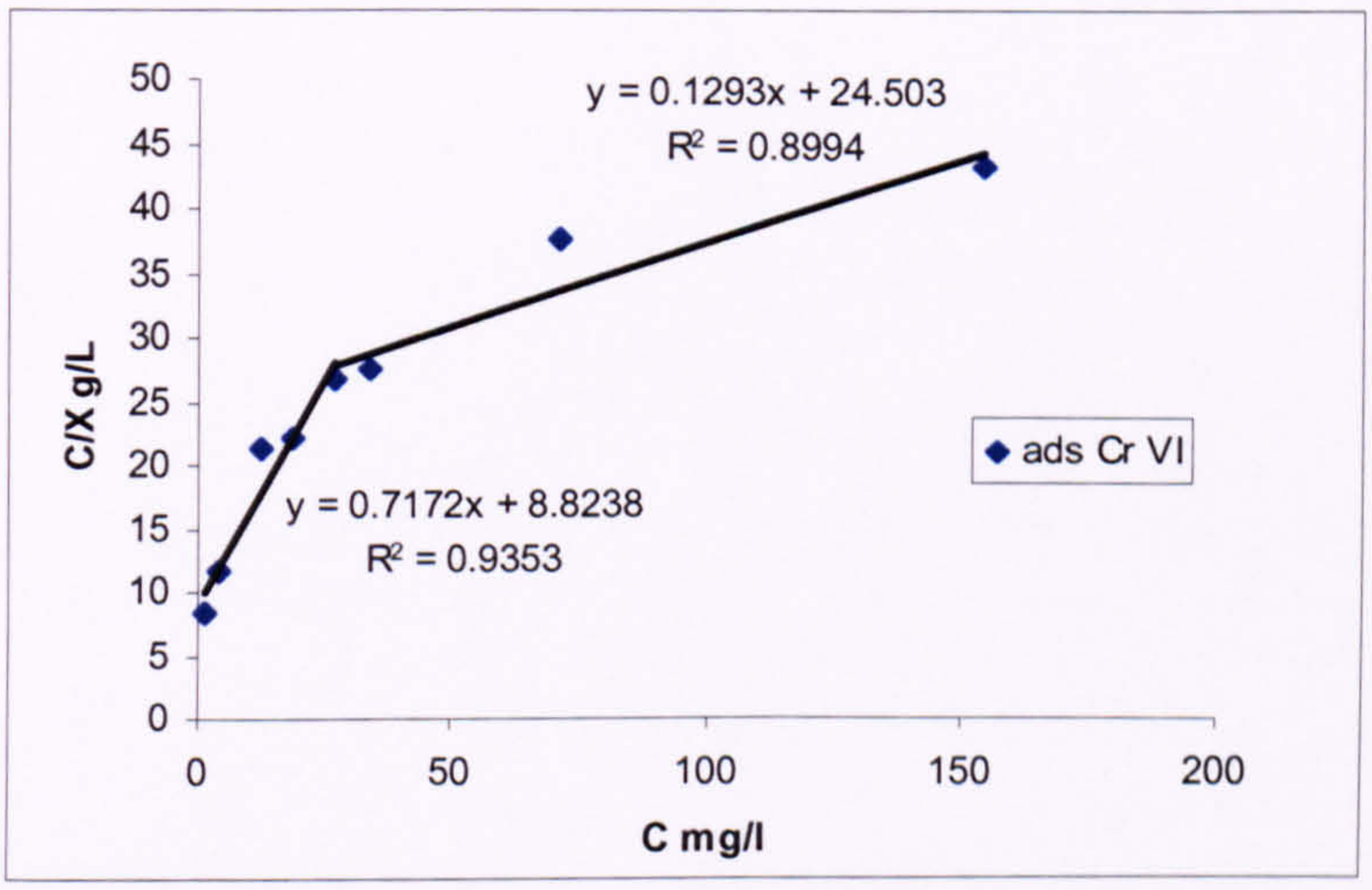
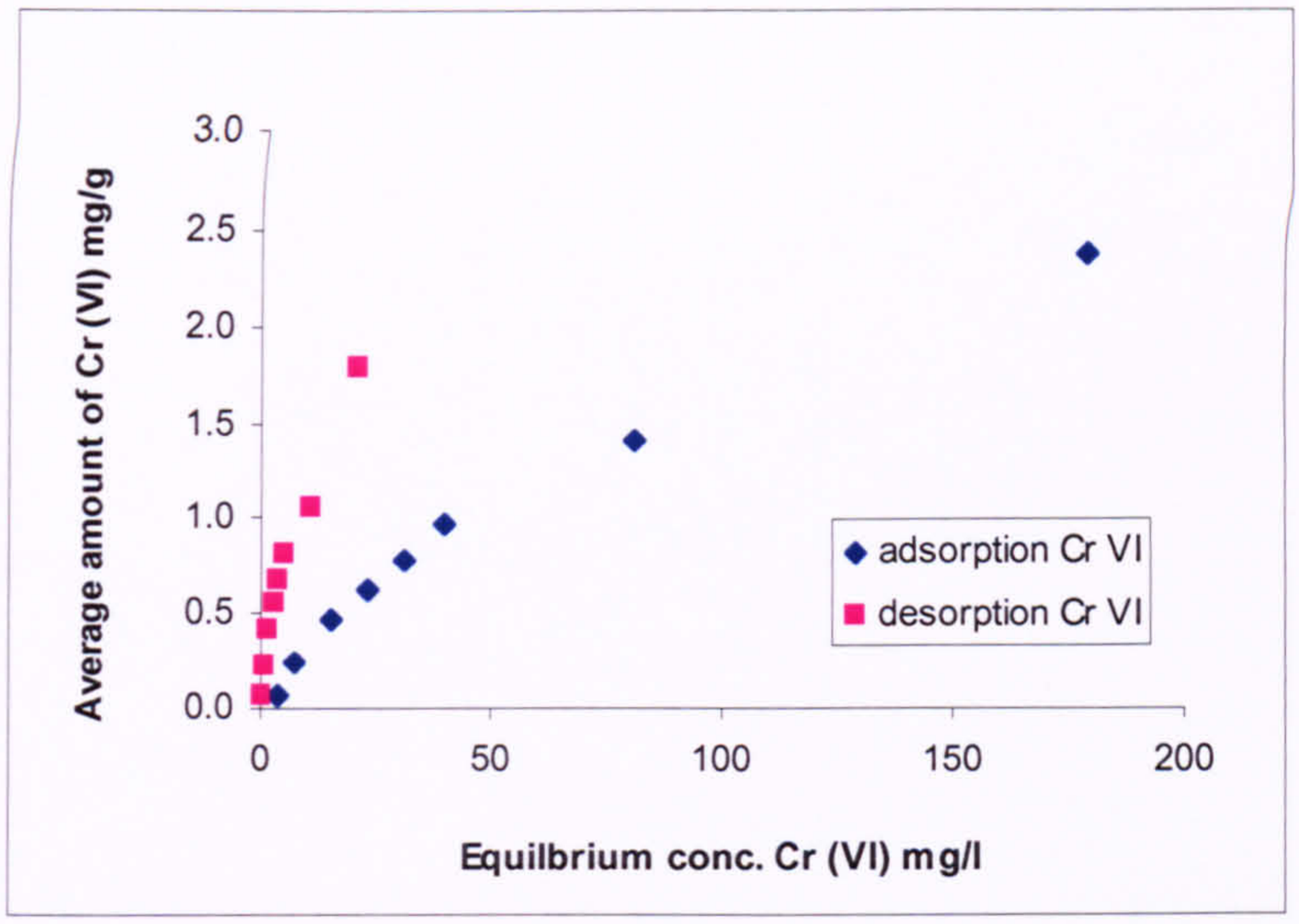


Figure 6-11 Langmuir isotherm for Cr (VI) adsorbed on Peat.



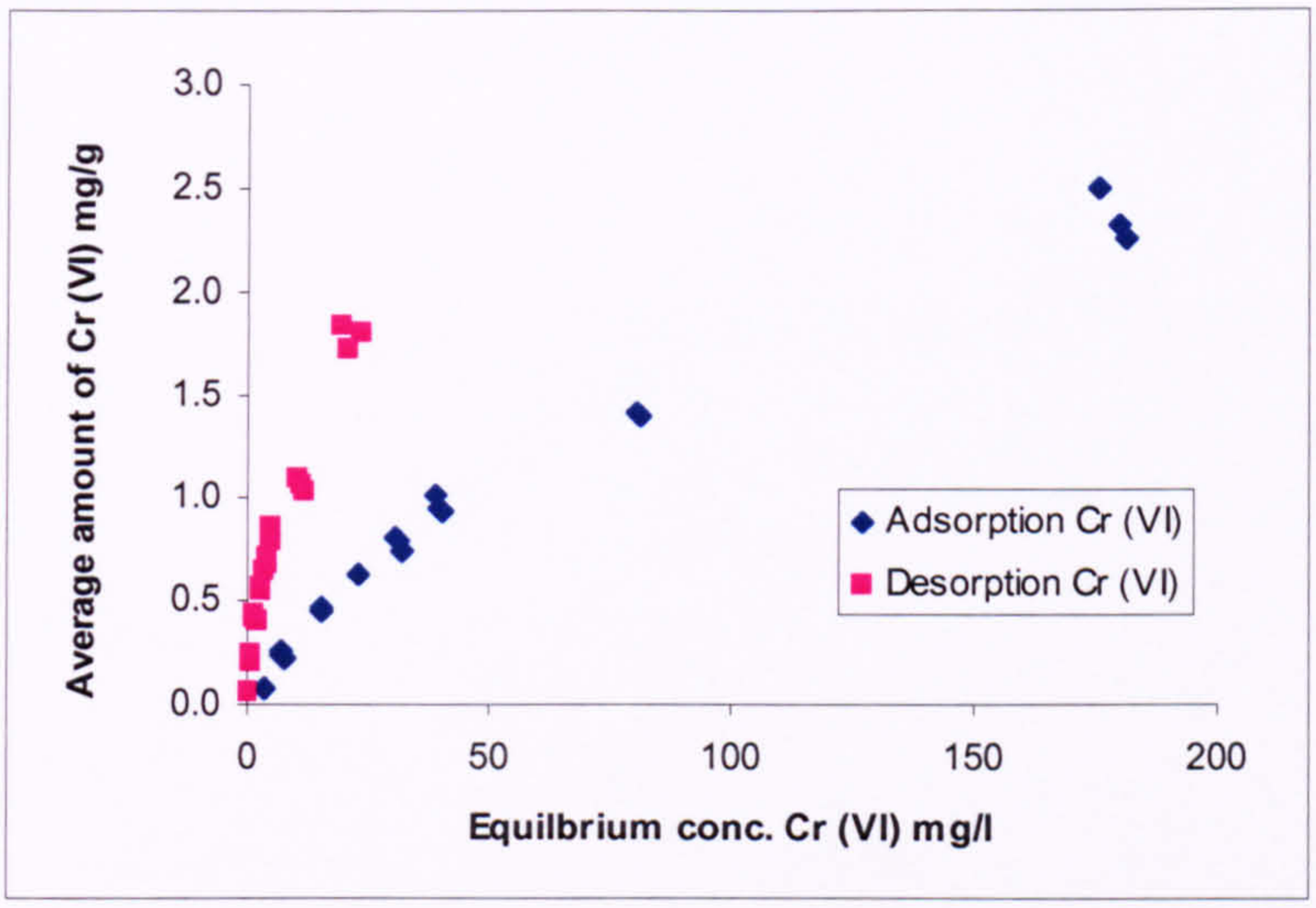


Figure 6-12 Adsorption - desorption the mean of Cr (VI) concentration and the replicate by Coir.

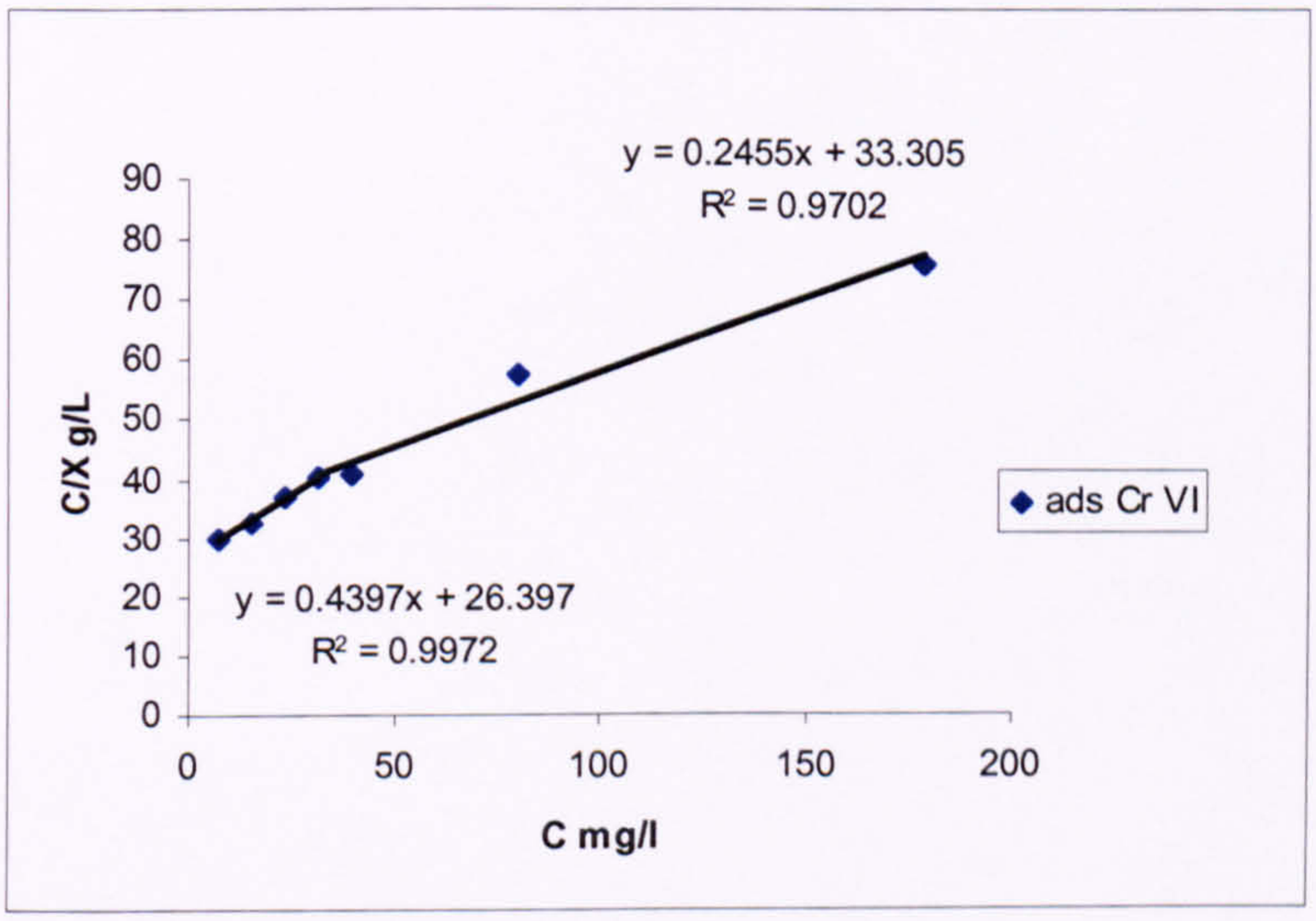


Figure 6-13 Langmuir isotherm for Cr (VI) adsorbed on Coir

Previous studies have suggested that the mechanism of Cr (VI) removed from aqueous solution by biomaterial or biomaterial-based activated carbons was anionic adsorption. However, it has been proved that Cr (VI) is easily reduced to Cr (III) by contact with organic materials under acidic conditions because of its high redox potential value (above +1.3 V) (Park et al., 2006). During the Cr (VI) reduction, some of the organic carbon of the biomass was completely oxidized into inorganic carbon (HCO_3^- and CO_2). Therefore, there is a strong possibility that the mechanism of Cr (VI) removal by biomaterial is adsorption coupled reduction (Babel and Kurniawan, 2003; Park et al., 2006). The carbon surface of the biomaterial contains carboxylic and hydroxyl groups, which play a role as electron donors (Bolan et al., 2003). Consequently, Cr (VI) oxyanion is readily reduced to Cr (III) ions due to the presence of electron donors on the organic matter. The increase in the concentration of potentially accessible carboxyl site due to surface oxidation has been clearly demonstrated by the increase of Cr adsorption capacity in the isotherm studies (Babel and Kurniawan, 2003).

Park et al. (2006) has revealed that Cr (VI) can be removed from the aqueous solution by nonliving biomass through following two mechanisms direct and indirect reduction of Cr (VI). The direct reduction is Cr (VI) reduced to Cr (III) directly in the aqueous phase by contact with the electron donor groups of the biomass. The second mechanism (indirect reduction), however, consists of three steps (1) the binding of anionic Cr (VI) ion species to the positively charged groups present on the biomass surface; (2) the reduction of Cr (VI) to Cr (III) by adjacent electron donor groups; (3) the release of the Cr (III) ions into the aqueous phase due to electronic repulsion between the positively charged groups and the Cr (III) ions, or the complexation of the Cr (III) with adjacent groups capable of Cr-binding (Park et al., 2006). This might explain the difference in adsorption capacity of Cr (III) and Cr (VI) on the carbon surface and why Cr (VI) is easily desorbed from the carbon surface.

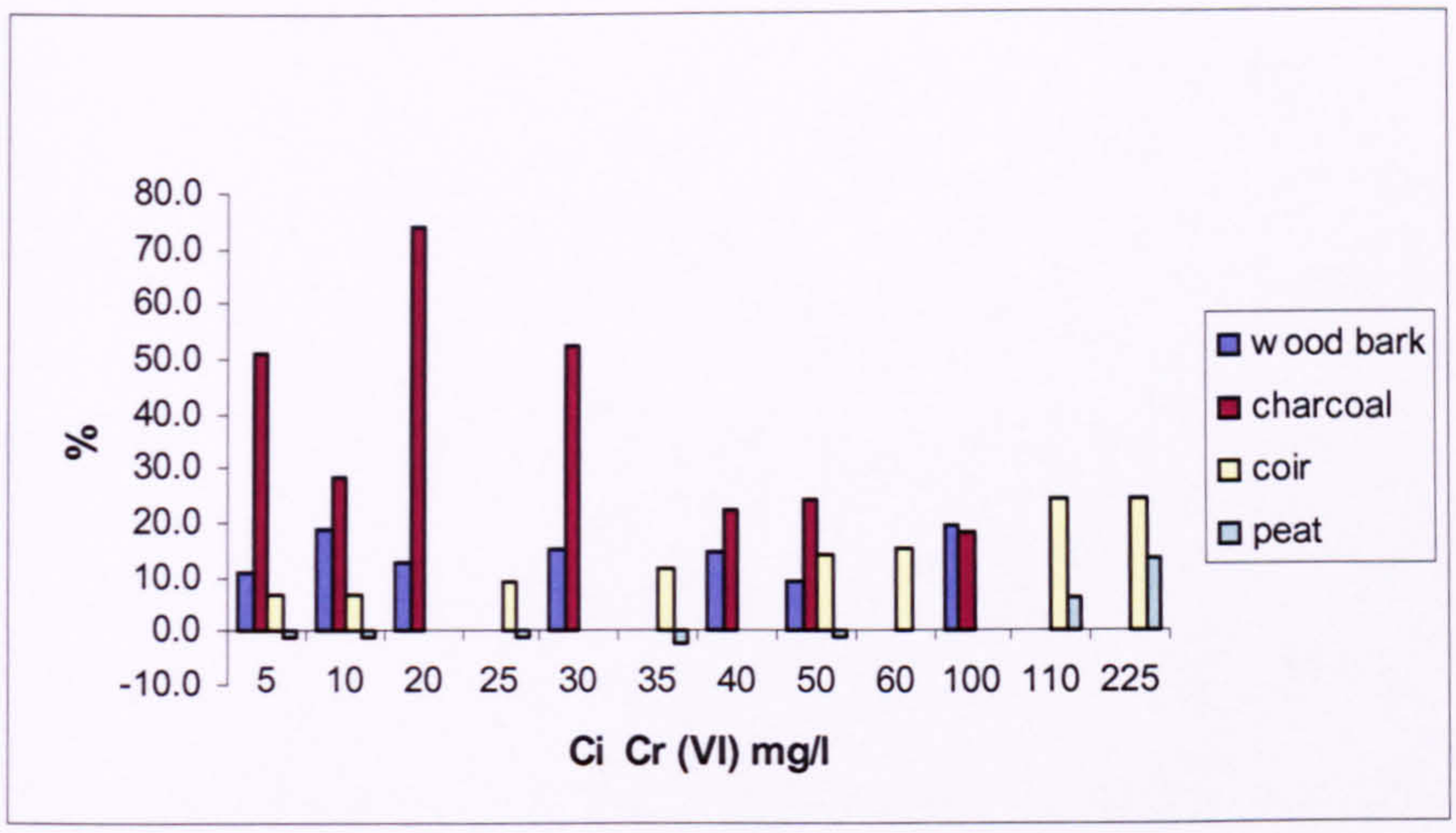


Figure 6-14 Percentage of Cr (VI) desorbed on each sorbents

The percentage of Cr (VI) removal was calculated as Equation 2.8 (Chapter 2). The different percentages of Cr (VI) removed are attributed to difference in the micro and macro structures of the adsorbents (Figure 6.14). The adsorption of Cr (VI) is controlled by two diffusion steps from the bulk solution to the adsorbent surface (outer sphere) and from the surface to the internal sites (inner sphere) and binding of the metal ions to the active sites (see Section 1.8.3.1.) (Dakiky et al., 2002).

Table 6-1 Summary of isotherm method

Type of Sorbants	Percentage of Cr (VI) % desorbed at 50 mg/l	Langmuir Theoretical capacity X_{max} mg/g of Cr (VI)	R^2	Langmuir Theoretical capacity X_{max} mg/g of Cr(III)	R^2
Peat	-1.3	LP* 1.39 HP* 7.73	0.9353 0.8994	NA*	NA*
Coir	13.7	LP* 2.27 HP* 4.07	0.9972 0.9702	NA*	NA*
Charcoal	24	NF*	NF*	9.37	0.9045
Wood bark	9.2	NF*	NF*	5.21	0.9851

***NA: Not available, NF: Not fit, LP: low concentration points, HP: High concentration points**

For the most of the sorbents, removal was almost complete at low chromium concentration, as seen by the steep rise in the isotherm before a slower approach to equilibrium at higher chromium concentrations. The capacity of chromium adsorbed in each sorbent is summarised at Table (6.1). Charcoal has highest capacity, which would suggest chromium is removed rapidly from solution, but is not held strongly to the charcoal with over 24 % desorbed at 50 mg/l initial concentration. This is evidence that ion exchange is involved in the adsorption process (Kadirvelu et al., 2001). The percentage of Cr (VI) desorbed from peat was –1.3 %, indicating that more chromium had adsorbed. Wood bark on the other hand has a slightly lower capacity but chromium was held by wood bark more strongly than the bone charcoal, about 9.2 % of Cr (VI) was desorbed at 50 mg/l initial concentration (Table 6.1). Coir too had a high percentage of Cr (VI) desorbed back in to solution. It was decided at this stage to continue with use of bone charcoal and wood bark for further studies.

Recently, various low-cost adsorbents derived from agricultural waste, industrial by-products or natural materials, have been investigated intensively for Cr (VI) removal from metal contaminated wastewater (Table 6.2). It is evident from the literature survey of

recent papers that after chemical modification or conversion by heating into activated carbon, low-cost adsorbents from agricultural waste have great potential removal capability for Cr (VI). It is important to note that the chromium adsorption capacities of low-cost adsorbents presented in Table (6.2) depend on the characteristics of the individual adsorbent, the extent of surface modification and the initial concentration of adsorbate (Babel and Kurniawan et al., 2003; Kurniawan et al., 2006).

Table 6-2 Low- cast adsorbents and activated carbon utilized for removal Cr (VI) by adsorption.

Source of adsorbent	Type of adsorbent	Optimum pH	Initial Cr (VI) concentration (mg/l)	Adsorption capacity (mg/g)	Reference
Agricultural waste	As-received CSC	6.0	20.0	2.18	(Babel and Kumiawan, 2004)
	CSC	4.0	20.0	3.65	
	CSC coated with chitosan	6.0	20.0	4.05	
	H_2SO_4-treated CSC	4.0	20.0	10.88	
	HNO_3 -treated CSC				
	Sawdust	2	100	15.82	Dakiky et al. (2002)
	Maple sawdust	5	10	5.1	(Yu et al., 2003)
	Hazelnut shell	10	1000	170	(Kobya, 2004)
	Activated alumina	4	10	1.6	(Bishnoi et al., 2004)
	Almond husk	5	250	37.17	(Hasar, 2003)
	Almond shell	2	100	10.62	(Dakiky et al., 2002)
	Ethylenediamine-modified rice hull	2	301.6	23.40	(Tang et al., 2003)
Industrial by-products	Bagasse	6	100	0.03	(Rao et al., 2002)
	Fly ash	6	90	0.01	(Ghosh et al., 2003)
	Hydrous titanium oxide	1.5	0.1	30.0	
Natural material	NaCl-treated zeolite	4.5	20.0	3.23	(Babel and Kurniawan, 2003)
	As-received zeolite	4.5	20.0	1.79	
	Pyrite fines	5.0-6.5	100	10.0	(Zoubulis et al., 1995)
	woolastonite	2.5	10.4	0.5	(Sharma, 2003)
Miscellaneous adsorbent	Milled peat	4	200	30.16	(Dean and Tobin, 1999)
	Soya cake	1.0	44	0.28	(Daneshvar et al., 2002)
	Wool	2.0	100	41.15	
	Olive cake	2.0	100	33.44	
	Cactus	2.0	100	7.08	(Dakiky et al., 2002)
	Pine needles	2.0	100	21.50	
	PVP-coated silica gel	4.5-5.5	10.0	3.5	(Gang et al., 2000)
Activated carbon	GAC type Filtrasorb 400	2.5-3.0	NA	145	(Sharma and Forster, 1996)
	As-received ACF	NA*	NA	2	(Shim et al., 2001)
	H_2SO_4- oxidised GAC	4.0	20.0	8.94	(Babel and Kurniawan, 2004)
	As- received GAC	4.0	20.0	4.72	

***NA: Not available, CSC: coconut shell charcoal, GAC: granular activated carbon, PVP: poly 4-vinylpyridine.**

6.4 Leaching of Cr (VI) through charcoal Columns

6.4.1 Introduction

Batch type processes are generally limited to the *treatment of small volumes* of contaminated solution, whereas fixed - bed systems can be used efficiently to treat larger quantities and continuous operation. In real - world applications for bone charcoal and wood bark flow-through, fixed bed columns can be utilised to remove Cr (VI) from industrial wastewater see Chapter 5. An adsorbent has a finite capacity for the substance it sorbs, as found in the above isotherm experiments (Section 6.2). Sorption isotherm could be used with successful scaling processes, however adsorption in column systems is not equilibrium due to the constant flow of fresh solution, so will not be comparable. The sorbent capacity as obtained from batch studies is necessary to determine the best dimensions for a column set up.

The fixed-bed adsorbers in practical concept is expressed in graphical terms by the breakthrough curve concept. As fluid is passed through a fixed-bed of adsorbent at entrance of the bed the initial transfer of adsorbate molecules from the feed to the solid occurs. Once the sorbent in this region becomes saturated, the zone in which mass transfer occurs moves progressively through the bed. If the effluent concentration is plotted as this occurs it illustrates an S-shaped curve in the adsorption zone with ends asymptotically approaching zero and the influent concentration, as shown in Figure 6.15. The area where sorption is occurring is termed the mass transfer zone (MTZ). The sorbent is saturated above the MTZ while below the MTZ sorption has not occurred, (Corbitt, 1990). To design a full-scale column systems the shape of the breakthrough curve, length of time until breakthrough occurs and the variables affecting are necessary to be known (Drose and Ronald, 1997; Lopez et al., 1998; McKay, 1996). It is very useful to be able to predict

when an effluent will 'breakthrough' a column so that an appropriate system can be designed to maintain consent conditions for as long as possible. The main factors affecting sorption are linear velocity, kinetics and initial concentration (Cheung et al., 2001b; Cooney, 1999).

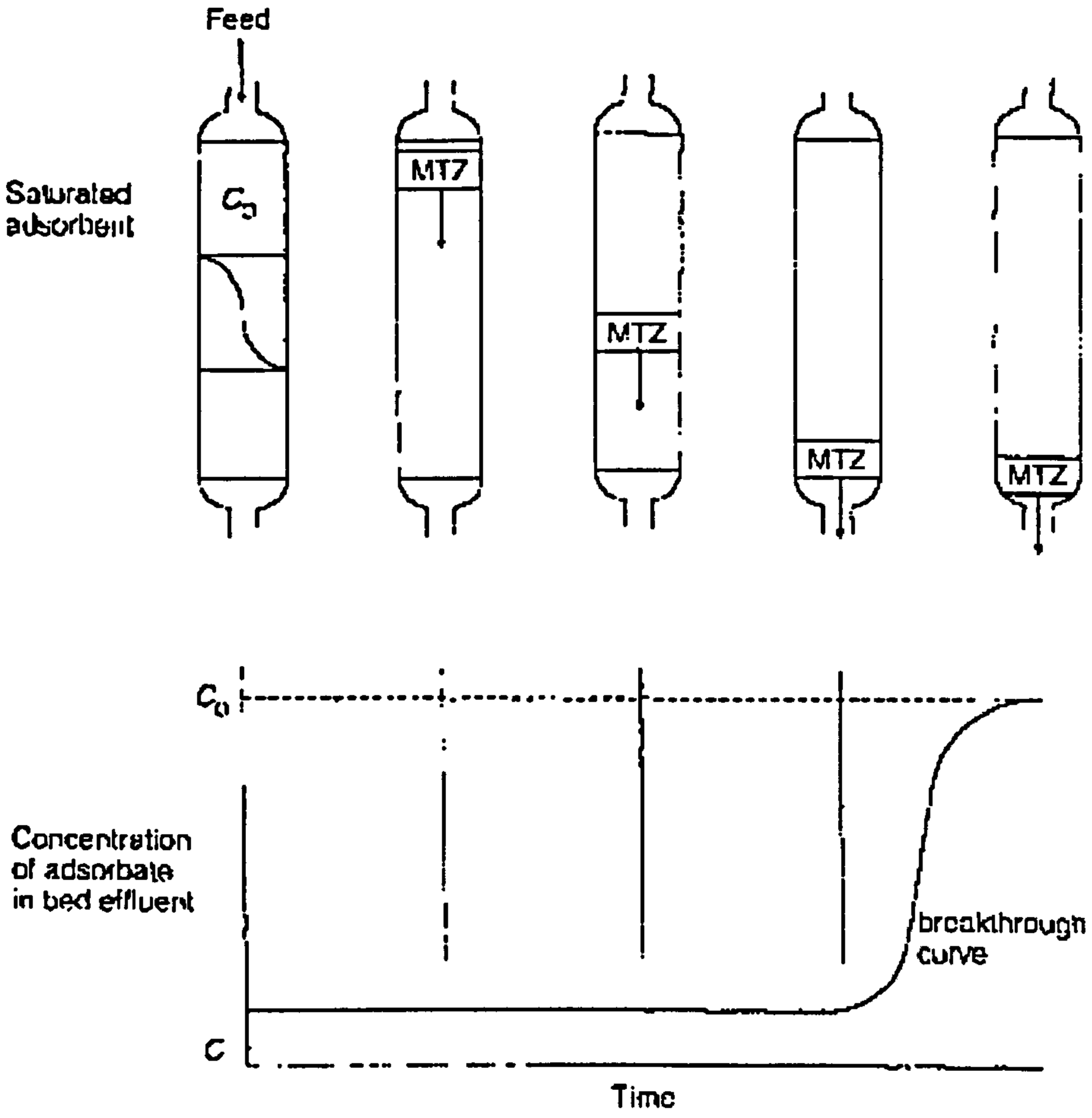


Figure 6-15 Schematic diagram showing the concentration profile, mass transfer and breakthrough curve in packed bed adsorption ((Crittenden et al., 1992), Section 4.19).

The mass transfer zone can be examined by simply measuring the effluent concentration over time. Columns were set up to carry this out. Plotting of the breakthrough curve and subsequent calculation allows the mass transfer zone length (MTZL) to be obtained. In its

most simplicity terms it is possible to design a fixed sorption bed by adding together the lengths corresponding to the amount of sorbent required for sorption based on the Langmuir maximum capacity and the MTZL. The mass transfer zone length, and therefore shape, is different with differing concentrations and column lengths. Apparently employing the technique, in real world terms, there is a need for excessively long columns as the breakthrough point is usually considerably before the mass transfer zone has exited the column.

6.4.2 Methods

Columns were set up according to the method outlined in Chapter 2 (Section 2.10.1). Three columns of different diameter were used. The mesh size of bone charcoal used here was 20 - 60 mesh. 5 and 10 g of dry charcoal was placed in columns of 26.6 mm width and 29 cm length of 2 and 4 cm bed length respectively. 50 g of charcoal was placed in column of 51.9 mm width 26 cm length 4.5 cm bed length. 1litre of chromium solution of 13.5 mg Cr/l initial concentration as K_2CrO_4 was passed through each column using gravity feed at a flow rate of 600 ml/h (Figure 6.16). Samples were collected in plastic bottles every 10 min, where they were stored until further analysis using AAS.

The batch experiment found that a high percentage of Cr (VI) was desorbed back to the solution from charcoal. This means charcoal might be difficult to apply to column leach of Cr (VI). As known from Wilson's work, charcoal could adsorb Zn well from solution, so Zn was taken as a comparison metal (Wilson, 2002).

The same system as above had been set up with Zn solution for comparison between the adsorption of Cr (VI) and Zn with charcoal. Column was leached with 1liter of 44 mg Zn/l

($Zn(NO_3)_2 .6H_2O$) with 5, 10 or 50 g charcoal, and a flow rate of 400 ml/h. Samples were collected every 20 min.

Results are expressed as percentage decrease in chromium solution concentration

$$\frac{\text{Outflow [Cr]}}{\text{Inflow [Cr]}} \times 100$$

Figure 6-16 Column leach system

6.4.3 Result and discussion

The experiment of chromium leach through columns of bone charcoal found that a column of 5 g of bone charcoal had no effect. Small effect was found with 10 g charcoal, the Cr (VI) concentration was decreased by about 10 %, but the 50 g charcoal had big effect, with the concentration decreasing to about 25 % initially, then stabilising at about 60 % of the original concentration, as mentioned above Section (6.4.1.) may be due to the different bed length so increasing the residence time therefore different breakthrough curve was found, or may be there is no enough time to reduce Cr (VI) to Cr (III) by the organic matter and adsorbed on to bone charcoal surface (Figure 6-17).

When Zn solution of 44 mg Zn/l was added to 5 g column of charcoal in the first 100 ml of Zn concentration fell to 0.27 % of the original and after 1 litre of Zn solution passed through the column it was 56 % of the original. For the 10g column, 0 % of Zn was detected from the first 400 ml leachate but after a 1 litre was leached Zn concentration fell to 16 % of the original. For the 50 g column there was no Zn detected in the effluent, which means Zn was totally removed from the solution (Figure 6.18).

In contrasts, the 5 g column of bone charcoal having the same bed length therefore have the same residence time for Cr (VI) and Zn, found no chromium was removed bout with Zn about 56% was removed before reach to the breakthrough point although with higher concentration. On 10 and 50 g bone charcoal with same bed length and residence time found slightly removal of Cr (VI) bout a good breakthrough curve with Zn for the 10 g column, and 25 % of Cr (VI) was initially removed but did not reach to the saturated point, and Zn was entirely removed and breakthrough point did not reach after 1 litre leached at the 50 g column.

Apparently the ability of charcoal to adsorb Cr (VI) was not good compared to Zn. Also desorption of Cr (VI) might be affecting the ability of charcoal to continue adsorbing Cr (VI). Although from these early studies charcoal looks promising as a sorbent for Cr (VI), when translated to a flow through system in fact it is not a good sorbent. Particularly comparing Cr (VI) uptake with Zn, which is good. So these works could not achieve the idea of fixed bed of charcoal to adsorb chromium.

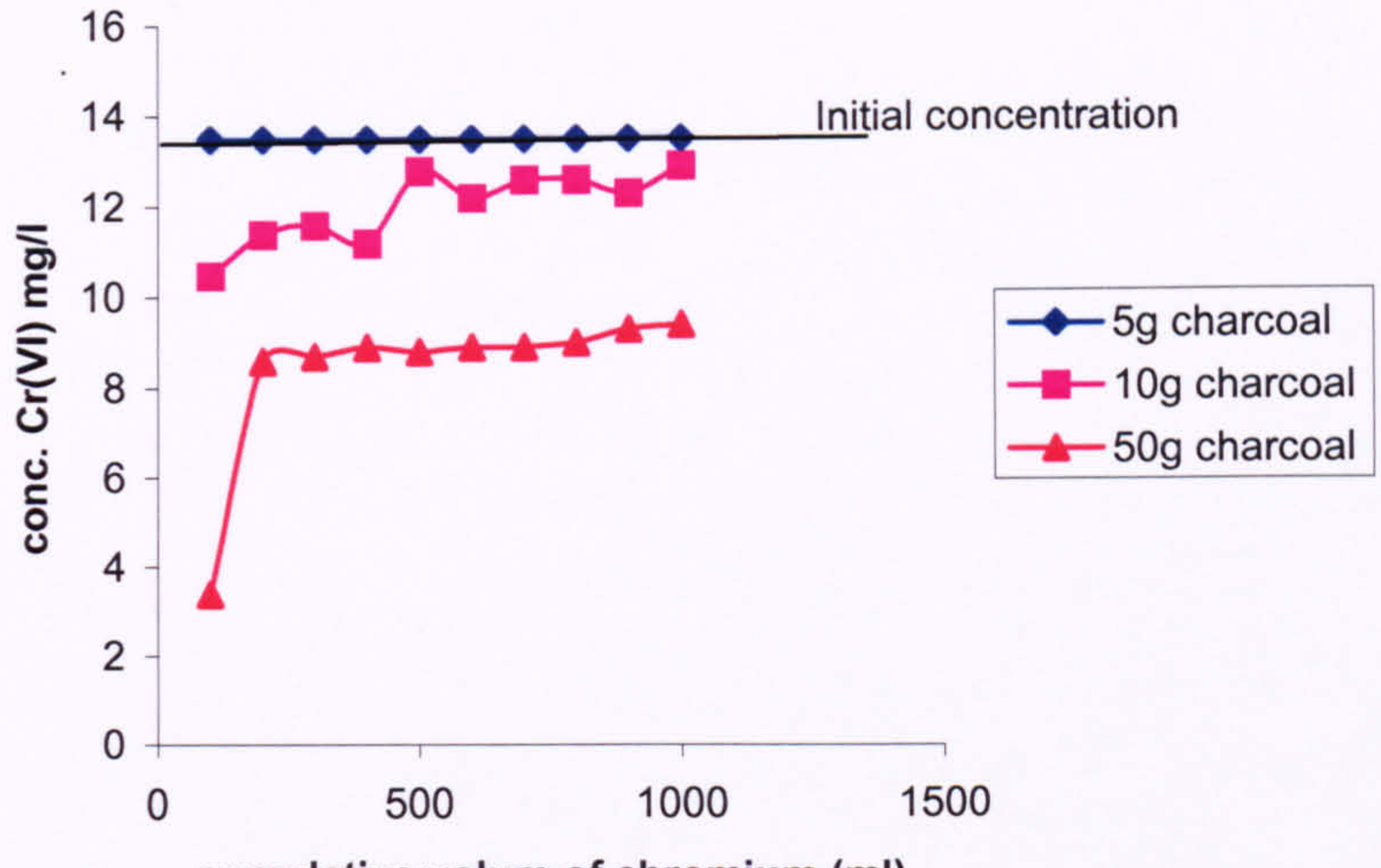


Figure 6-17 Cr (VI) concentrations in solution following leaching of a 13.5 mg Cr/l solution through columns of different amount of charcoal

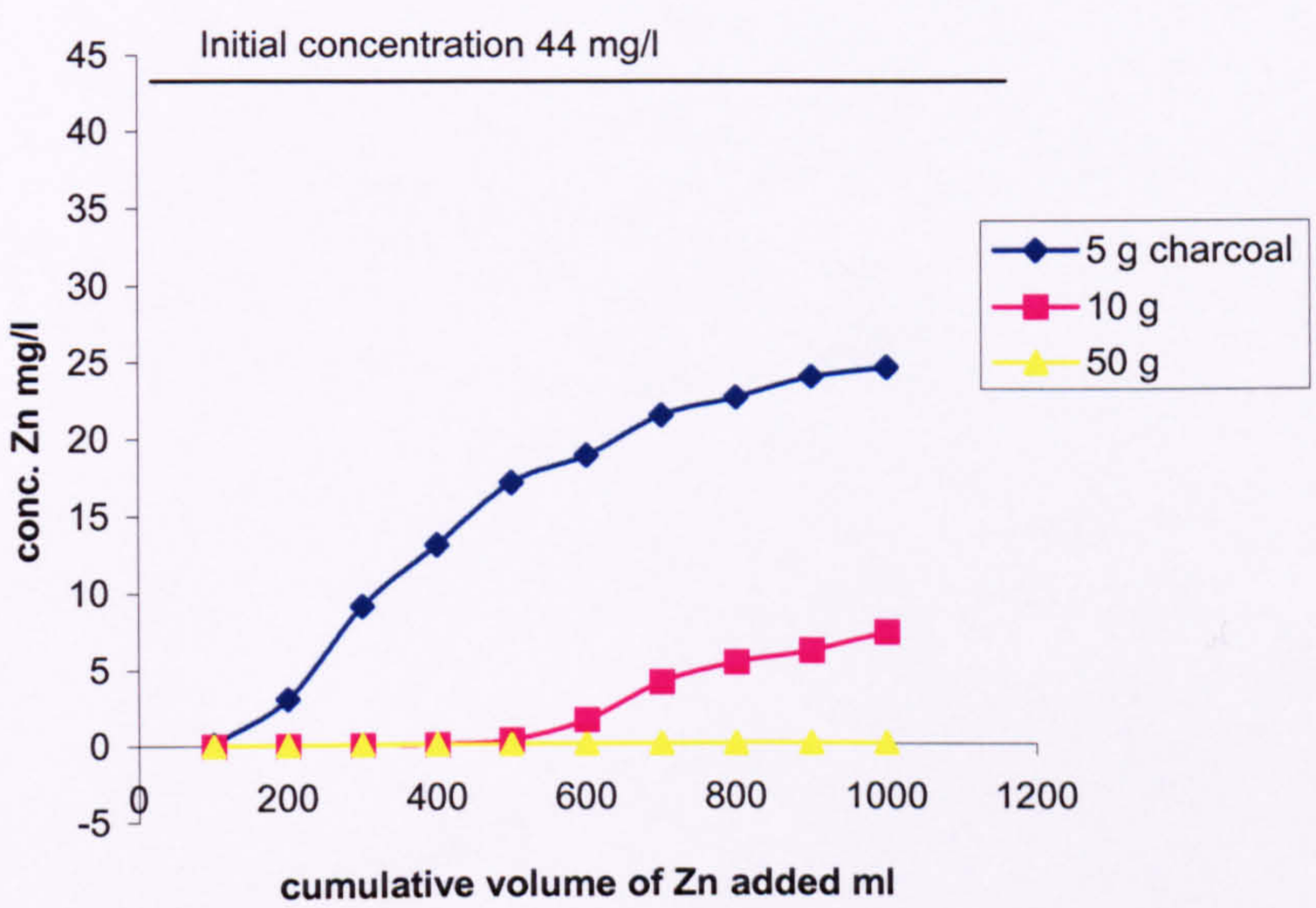


Figure 6-18 Zn concentrations in solution following leaching of a 44mg Zn/l solution through columns of different amount of charcoal

6.5 Effect of interaction time on adsorption of chromium by wood bark

6.5.1 Aim

The aim of this experiment was to obtain a capacity for the amount of Cr (VI) to be sorbed by wood bark with different shaking times.

6.5.2 Method

The basic method set out in Chapter 2 (Section 2.9.2.2.) was used. 50 ml solution of 5 mg/l Cr (VI) was added to 1 g of wood bark then shaken for varying times (5, 15, 30, 60, 120, 180, 240, 300, 360, and 420 min), then filtered and samples analysed by AAS. The chromium concentrations were measured both in initial solution and after adsorption. All was run in triplicate.

6.5.3 Result and Discussion

Results of wood bark capacity to adsorb chromium within different contact times are shown in Figure 6.19. Adsorption of chromium initially was rapid with more than 40 % of total amount removed within the first 60 min of the process. Thereafter the rate of adsorption was slower. Adsorption stabilised at about 90 % after about 300 minutes.

There was rapid uptake of chromium, as within 60 min over 40 % removal of the chromium from solution had occurred. Over 60 min, uptake of the chromium was slower but gradually increased. Therefore increasing the interaction time between wood bark and chromium solution has an influence on the amount of chromium adsorbed. This suggested

the contact time has to be a concern in the flow through system, as observed from this experiment. Dakiky (2002) studied the effect of contact time on batch adsorption of Cr (VI) with low cost sorbent found that the increase the contact time increased the percentage removal of Cr (VI) and also revealed that the nature of the adsorbent and its compactness affected the time needed to reach equilibrium.

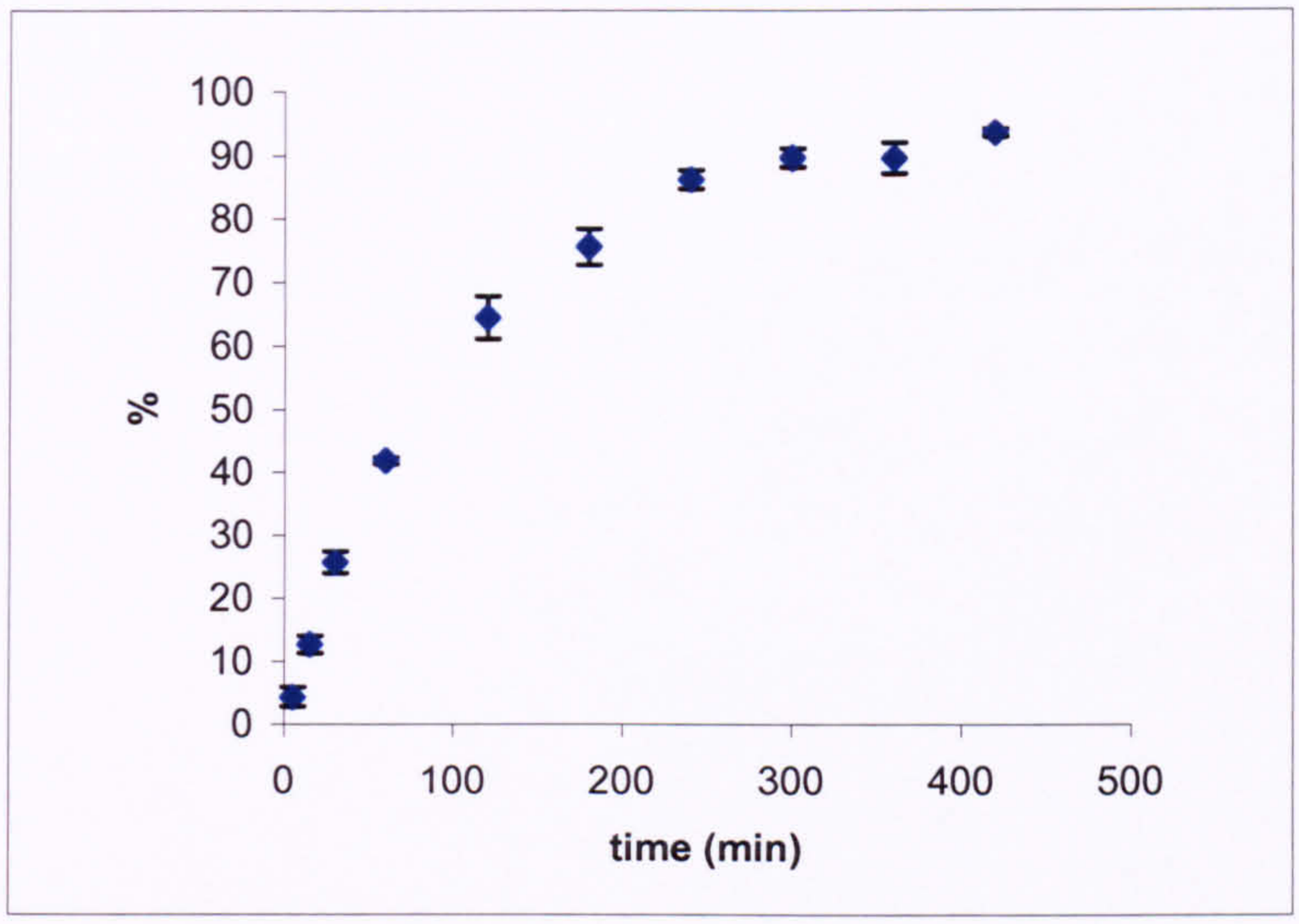


Figure 6-19 Percentage adsorption of chromium with time

6.6 The study of chromium adsorbed by different particle size of wood bark

6.6.1 Aim

The previous experiment found that the contact time affects the wood bark capacity to adsorb chromium from solution. In order to examine the capacity of wood bark aspect more clearly, adsorption isotherm of Cr (VI) was determined on different particles size of wood bark.

6.6.2 Method

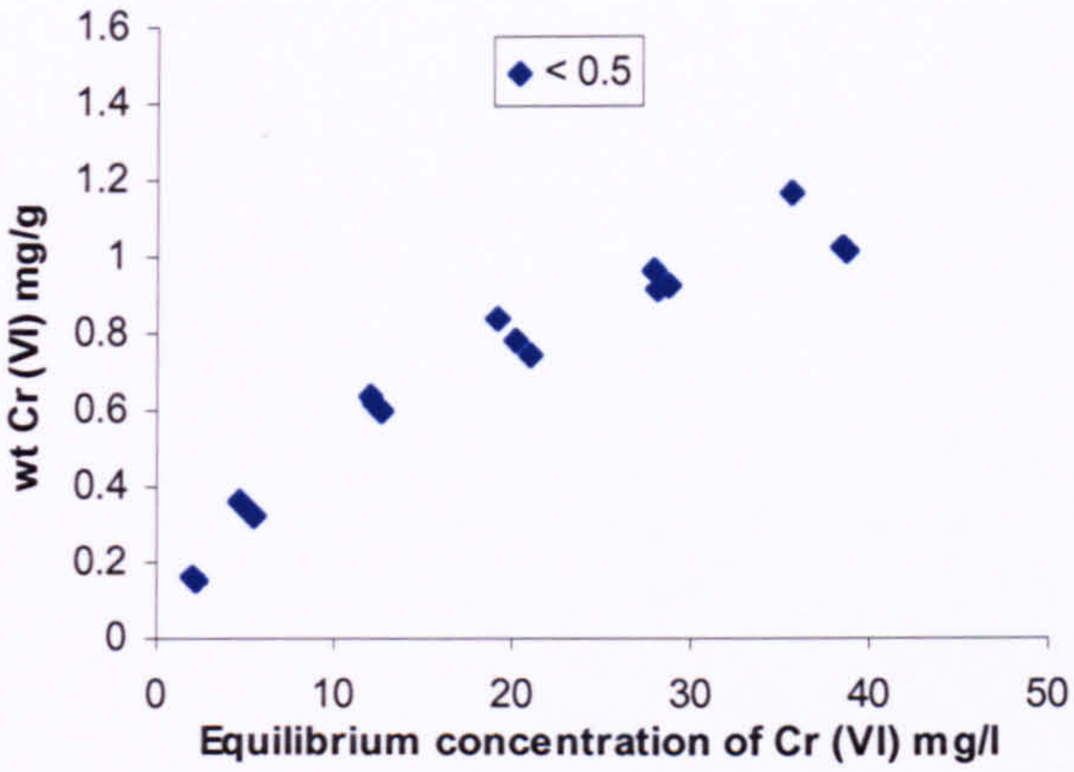
300 g of wood bark was sieved out in to three size sieves (4.0 mm, 2.8mm, 0.5 mm) to have four different particles size of wood bark (30 g (10 %) < 0.5 mm, 148 g (49%) > 0.5 < 2.8 mm, 25 g (8 %) > 2.8 < 4 mm and 100 g (33 %) > 4 mm) was a maximum particles size of 3-5 cm. 1 g of each particles size was weighted in triplicate then 50 ml of Cr (VI) solution of varying concentration, 5, 10, 20, 30, 40, and 50 mg/l was added. These were shaken for 1h then filtered as previously in Section 2.9 and the equilibrium solution analysed by AAS.

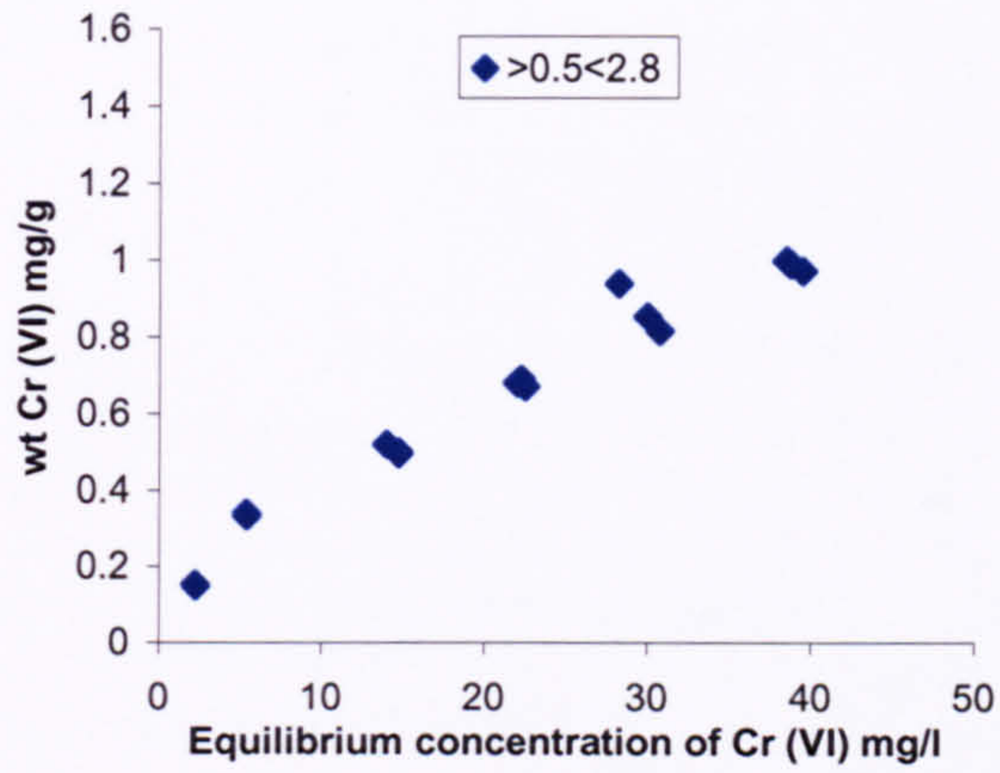
6.6.3 Result and Discussion

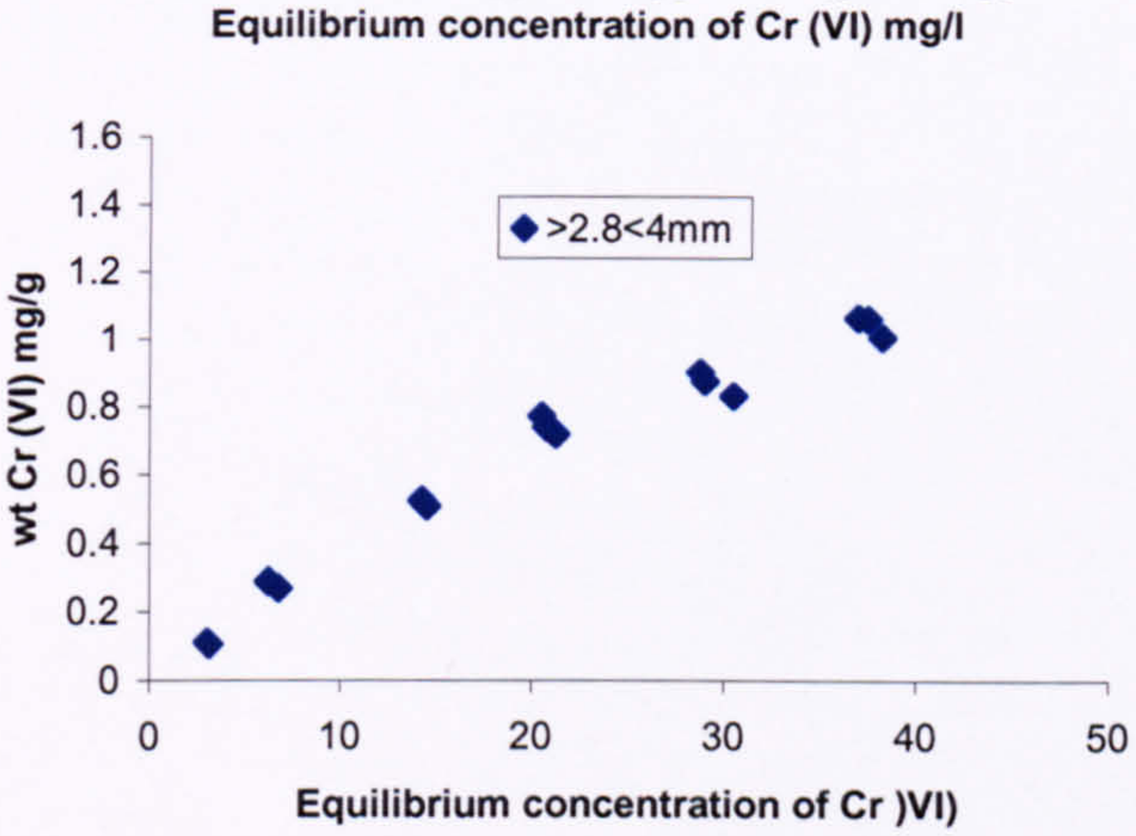
The effect of particle size on chromium adsorption was investigated over the range < 0.5, > 4 mm. Such data would be valuable for scale –up and for practical application in a fixed-bed column adsorption system. The aspect of size particle of wood bark does need to balance between the large and small materials in the flow system. The purpose of using all

size fraction of wood bark is for flow through properties. The needs of sufficient large materials of > 4mm to keep flow through open and sufficient small materials which is thought might be important in terms of adsorption amount, also needs this small materials to slow the flow rate.

Surprisingly, the experimental results did not show any significant difference in the amount of Cr (VI) sorbed between the different particle size fractions (Figure 6.20). Although, samples of 1g of the small or intermediate particles size were mainly uniform, so this allowing easier penetration of the Cr (VI) to the particle sites. But 1g of large material (>4mm) which is non-uniform, therefore the scatter at high concentrations may be due to problem of getting good replicates of such large material, limiting the surface sites exist to sorbed Cr (VI). In comparing these four different particle sizes of wood bark there were no visible differences in the ability to remove chromium, particularly at low chromium concentration (<30 mg/l). The result shows that there is no need to separate out the different size fractions of wood bark, so wood bark can be used as received for fixed-bed system. A similar result has been found with other adsorbents, for example the effect of particle size on arsenic adsorption by natural iron ores was studied and found that no any significant different of residual As (V) concentration over the all range of the investigated particle size (Zhang et al., 2004).







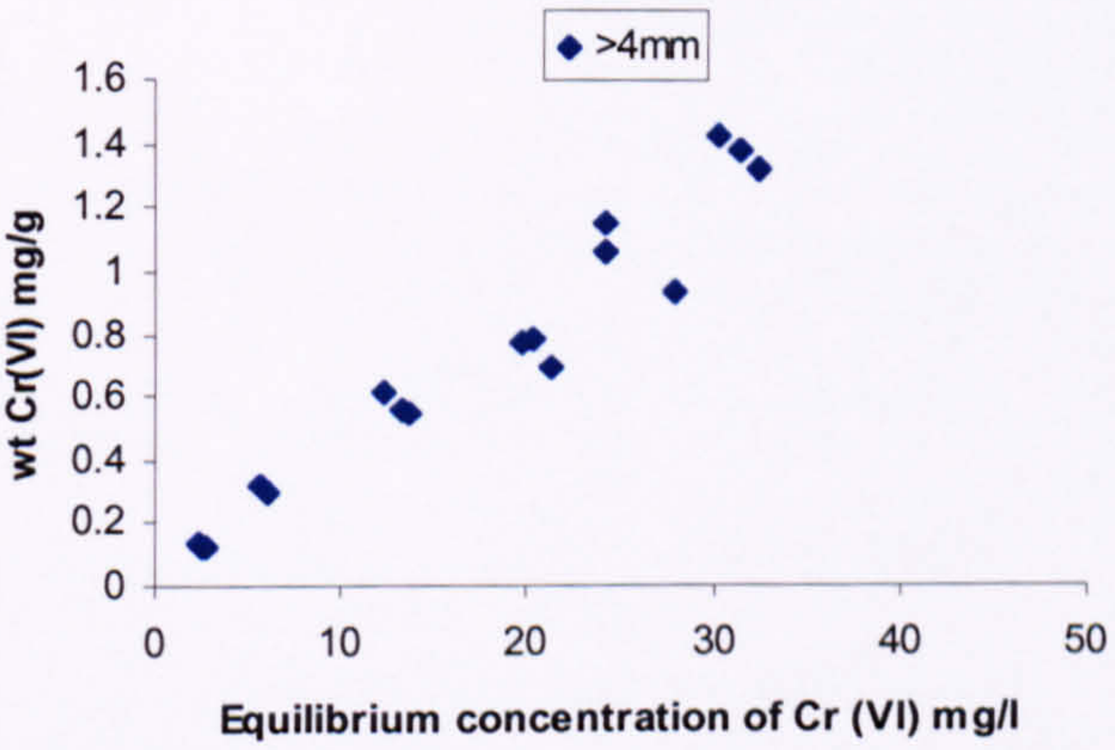


Figure 6-20 Adsorption of Cr (VI) by different particle size of wood bark

Shaking time experiment showed that with increasing the contact time the capacity of chromium removed from solution increased. It was particularly fast in the first 60 min and slower but gradual after that. Different particle sizes of wood bark all had a similar isotherm curve that means there is no effect of particle size on the capacity of Cr (VI) adsorbed. This information is useful to apply wood bark by column leaching system as an example of the real–world treatment.

6.7 Column system for removal of chromium by wood bark

The results of the previous two experiments found that uptake of chromium from solution increased with time and the different particle size had no effect. Therefore, the fixed bed was set up for four columns as in Chapter 2 (Section 2.10.1). Two columns of 51 mm diameter and length 26 cm were filled with 10 g of moist wood bark mixed with 1:1 acid sand, and two columns of 65.5 mm diameter and length 30 cm with 50 g of moist wood bark also mixed with 1:1 acid sand. Then 1 litre of chromium solution 5 mg Cr (VI)/l initial concentration as K_2CrO_4 passed through each column in two different flow rates using peristaltic pump to ensure constant flow 200 ml/h and 130 ml/h. the samples were collected in 100 ml aliquots.

6.7.1 Result and discussion

The results of column leaching of Cr (VI) by different amounts of wood bark at different flow rates are plotted in Figure (6.21). In columns with 10g of wood bark and a fast flow rate the amount of chromium leached was high, over 70 – 80 % from the original chromium concentration. With the slow flow rate the chromium concentration fell to nearly 11 % of the original in the first 100 ml but it gradually increased to over 70 % after

1 litre of chromium solution had been leached through the wood bark. In the column of 50 g wood bark only 50 % of the original chromium concentration was found in at the fast flow rate, but slow flow rate found virtually no chromium was detected in the leachate, that means wood bark removed all the chromium from the solution. So low amount of chromium removed from the solution with the fast flow rate, which might be due to the short interaction time. In terms of slow flow rate significant amount of chromium removed from solution, which is due to longer interaction time (Figure 6.21). Presumably, from the different amount of wood bark in a different column diameter and different flow rate will lead to different residence time therefore the breakthrough curve was different.

Maintaining the same contact time with different amounts of wood bark found different percentage of chromium adsorbed. This experiment concludes that the amount of wood bark and the contact time play an important role for removing chromium from solution. However, (Parab et al., 2006; Sarin and Pant, 2006) found that removal of hexavalent chromium from solutions was possible using eucalyptus bark, which removed more than 99 % of Cr (VI) at concentration of 200 ppm and at pH 2. Increase in the amount of adsorbent, initial concentration of Cr (VI) and increase in contact time up to 2 h all increased the adsorption of Cr (VI).

Therefore, next experiment was setup to study the influence of interaction time on to the amount of chromium adsorbed on to wood bark and the residence time before the breakthrough curve establish based on the design of the flow through system.

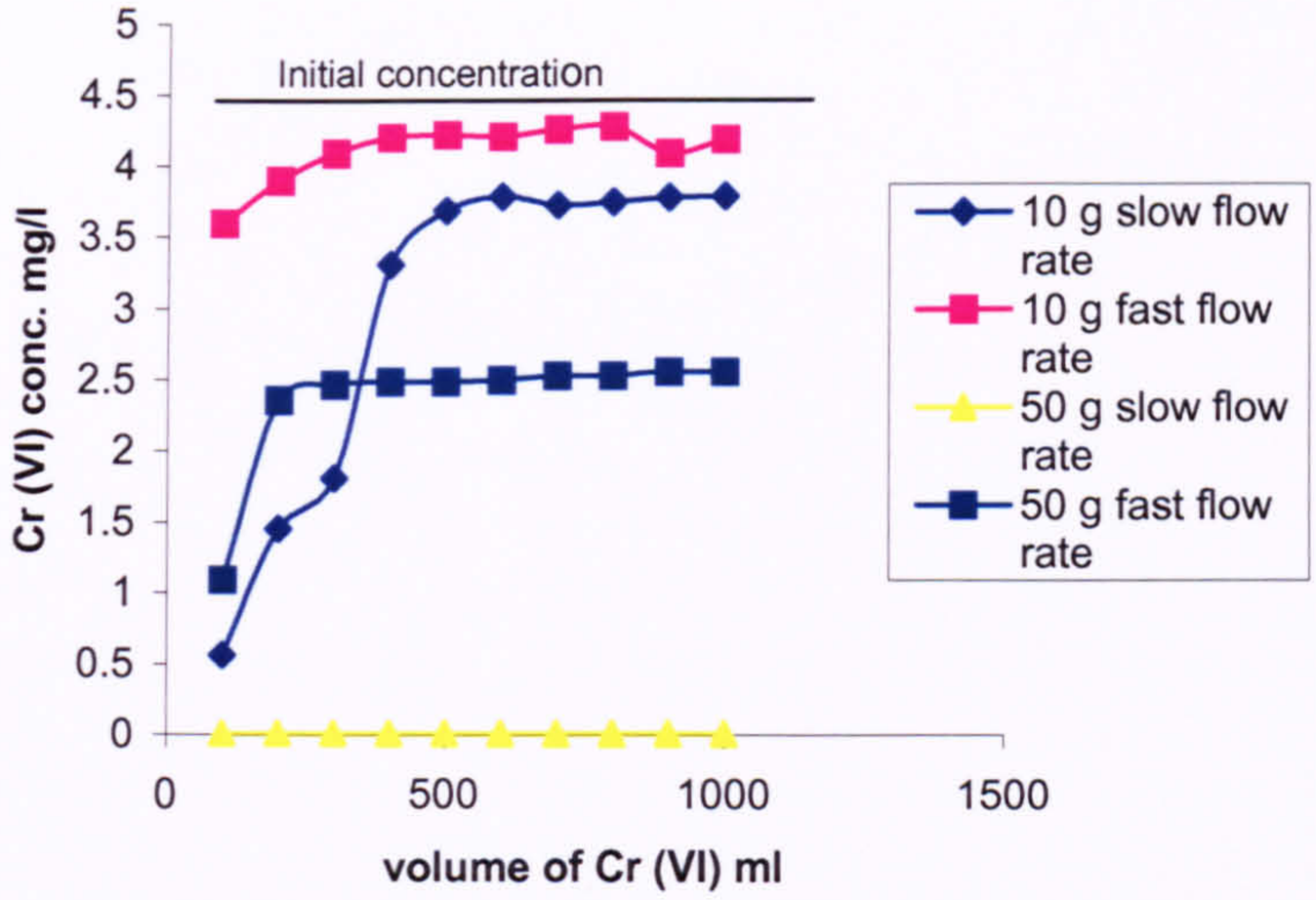


Figure 6-21 Cr (VI) concentrations in solution following leaching of a 5 mg Cr/l solution through columns of wood bark at different flow rates

6.8 The flow through system of chromium via bed of wood bark

6.8.1 Introduction

The concept of fixed-bed adsorbers is expressed in graphical terms by the breakthrough curve concept. The shape of breakthrough is usually an S-shaped curve. The length of time until breakthrough occurs and the variables affecting it are necessary to be known for design of full-scale column systems (Jenne, 1998). The design of a fixed-bed adsorber will be examined, in relation to two factors, the amount of sorbents and the contact time.

6.8.2 Flow through System

A longer-term system proved difficult to sample, due to length of time needed between samples and also the length of time the experiment needed to run. In this system 500 g samples of wood bark were washed to remove fine wood dust by washing several times in deionised water and then allowed to partially dry overnight. The 500 g of damp wood bark was placed in a 3 litre plastic container and covered with a fine grade of polyester mesh and then with 5 mm of sand to keep the bark in position. A reservoir containing 30 mg/l Cr (VI) was attached to one end of a peristaltic pump with a flow rate of (60 and 150 ml/h) the other end of the plastic tube was placed in the wood bark close to the bottom of the container to allow the chromium solution to percolate through the wood bark. The system set running to leach chromium solution, but the lag time before started to sample was the time needed for replacement of approximately 1 litre water already in the wood bark by chromium solution. The leachate was collected in batches of 100 ml every 24 h or 48 h for analysis by AAS (Figure 6.22 a). This system was repeated with 2500 g of damp bark in a

7 litre plastic container and the same initial chromium concentration (30 mg/l Cr (VI)) and two flow rates (60 and 150 ml/h) (Figure 6.22 b). The lag time here was for replacement of approximately 5 litre water before collecting samples. Each system was flushed with more than 150 - 200 litres of chromium solution.

In this experiment 30 mg/l Cr (VI) concentration was used based upon the chromium concentration in ground water were found at contaminant area in S.E. Glasgow (Farmer et al., 2002).

(a)

(b)

Figure 6-22 Flow through system picture (a) 500 g (b) 2500 g wood bark

6.8.3 Result and Discussion

6.8.3.1 500 g system

In the 500 g system of wood bark with 30 mg/l Cr (VI) solution leached through, all the chromium was removed from the solution up to a volume of 10 litres for the slow flow rate system, thereafter Cr (VI) concentration increased. At the faster flow rate, chromium was detected from the first leachate collected and continued to increase. At the slow rate system the equilibrium was around 12 mg Cr/l and the wood bark became saturated once 75,000 ml of Cr (VI) solution had been percolated through the system over 3 months. At the fast flow rate the system equilibrated about 20 mg Cr/l and wood bark became saturated above 50,000 ml of Cr (VI) solution passed through. This system was run over a month. Up to 120 litres of Cr (VI) solution had been leached in each system.

The slower the flow rates the longer the time to breakthrough so the difference is the contact time between the solution and the wood bark (Figure 6.23). A similar result was obtained using charcoal to adsorb Cr (III) in column system with two different flow rates, and it was observed that with the slow flow rate a longer time was taken to breakthrough (Wilson, 2002).

6.8.3.2 2500 g system

The system with 2500 g wood bark was run under the same conditions as above. The two systems had been run over 2.5 months. The amount of wood bark was 5 times more than the previous system. Cr (VI) was completely removed up to about 100 litres; this is 10 times more than the small system. There was still no breakthrough seen for chromium in terms of slow flow rate (Figure 6.24), suggesting the bed still has considerable total

capacity for chromium if it was to be run to exhaustion, but system did not run beyond this because of lack of time. The faster flow rate system reached the breakthrough above 130 litres of chromium solution leached through the wood bark, but the system did not run to equilibrium because of the time constraint. The two curves are much closer together in terms of the time taken to break through (Figure 6.24).

The objective from this system is to know how long Cr (VI) concentration in leachate could be maintained below the criteria of chromium concentration in water, with the amount of wood bark and the contact time before it reached saturation.

With the 60 ml/h system and 500 g wood bark, chromium was removed entirely by about 10 litres. The residence time for 500g systems of flow rate 60 ml/h and 150 ml/h approximately 16.5 h and 6.5 h respectively. If the amount of wood bark were increased 5 fold to the 2500 g, the expectation would be to remove chromium from solution with about 50 litres. In fact chromium removal continued to over 100 litres. This is double the estimation and 10 times more than the 500 g system, so it is not a simple conversion, and the approximately residence time for 2500 g system was 83 h of 60 ml/h flow rate and it was 33 h of 150 ml/h flow rate. Affectively, the least contact time for the smallest system was 6.5 h while on Section 6.5 studied the effect of interaction time on adsorption Cr by bark the maximum adsorption would be 90 % after 5 h (Figure 6.19), this means there is no chromium could leach before that time, although there is slightly different bout that could be because the first system is batch and the second system is flow through. Clearly that would give a conservative estimate of the time scale for use of a bigger bed. If 2.5 tons of wood bark is used instead of 2.5 kg, then we would expect chromium removal to at least a 100,000 litres of leachate, and may actually more could be removed based on the results of this experiment. This shows there is potential for using wood bark for long-term removal, but this work now needs to be developed to field scale.

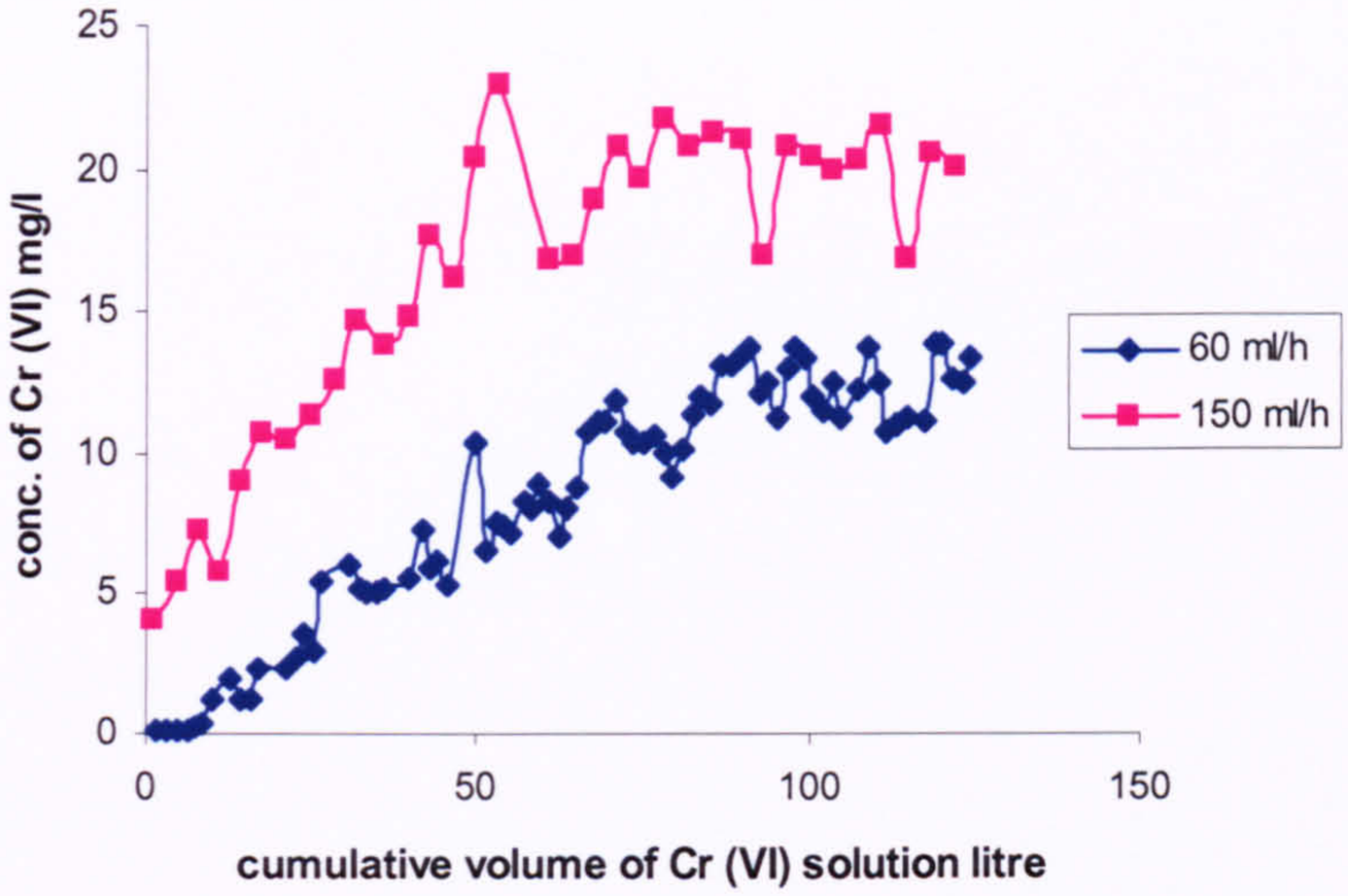


Figure 6-23 Cr (VI) leached from 500g wood bark with different flow rates

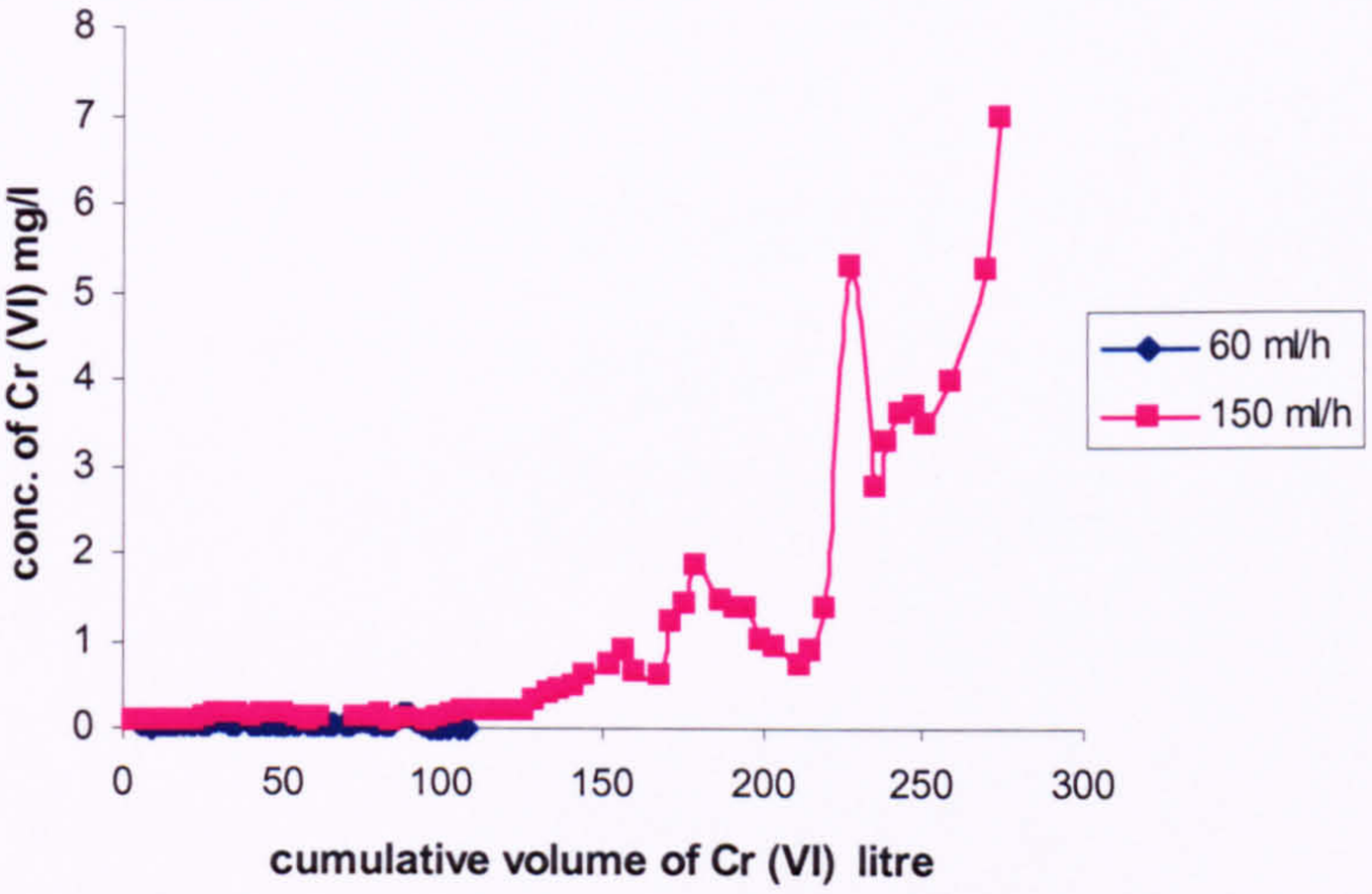


Figure 6-24 Cr (VI) leached from 2500 g wood bark with different flow rate

Chapter 7

General Discussion

This chapter integrates all the results that have been obtained in the previous chapters. It is known that in the Rutherglen area in S.E Glasgow there is an issue concerning the dumpsite of waste from a factory that processed chromium ore. Also there is evidence that this is acting as a source of contamination over a wide area of Glasgow. The results of the survey undertaken suggest there is a strong localised effect around former factory site, and also there is evidence of wider effect by wind blow, with a mean value of 60 mg/kg background in S.E Glasgow. This contrasts with mean of 30 mg/kg in N.W Glasgow.

The natural recovery processes could reduce the potential risk, but there is no any evidence that this will occur at a particular site. Potential exposure levels may be reduced by lowering of concentration levels by dilution or dispersion, or by excavation and dumping the waste in landfill sites but that could still present a great risk. These methods of treatment are unlikely to be suitable for high concentration levels of chromium and may require a long time to achieve their objectives (USEPA, 2000).

In terms of the pollution linkage model (see Section 6.1), to break the pathway for transmission to humans by inhalation or ingestion due to dust blow it will be necessary to cover it. Ideally the waste could be remediated chemically then vegetated. The evidence from SEPA (1999-2000) and Farmer et. al (1999) shows that chromium has been leached from the dumpsite to the groundwater eventually to River Clyde, which poses a much greater threat to plants and ecosystems. Breaking the leaching pathway to reduce the risk by remediating the groundwater and surface water using a bed of low cost adsorption materials may be the best solution. This project is concerned about these two pieces of

evidence of dispersal of chromium by wind blow and leaching. This area has now been developed there is need to treat both the waste and leachate from the waste in order to prevent further contamination of the environment.

The treatment of the waste material with a view to both reducing the risk from dust blow and the risk from leaching has been commonly done by using reduction by Fe (II). Fe (II) ions are known as a potential treatment to immobilise chromium by reducing Cr (VI) to Cr (III), which is less toxic, but if it is left un-vegetated there could be re-oxidation to Cr (VI).

An alternative treatment would be treating the leachate. One option might be to use Mn (II) which, as it is found in Chapter 4, may oxidise Cr (III) to Cr (VI), and mobilise the chromium then leach it and treat the leachate. This aspect needs to taken farther in conjunction with other remediation processes.

Treatment of chromium waste by Fe (II) reduction could be combined with phytoremediation to stop dust blow from the dumpsite, one potential remediation might be vegetation growing on the site to stabilise it (Bolan and Duraisamy, 2003; Banks et al., 2006), which is not dealt with in this thesis, but is an alternative treatment could that be applied.

The behaviour of chromium leachate from soil was discussed in chapter 5 and it was observed that there was an initial fast release of chromium, followed by a slow release. When looked at in detail with intermittent leaching (Figure 5.6) there was an increase in chromium concentration in the leachate after a dry period, which will mirror what could happen in the environment. Presumably the chromium leaching from soil depends on the dry and wet periods. Therefore, in the wet period it would be expected that more chromium leachs out of the soil in the initial pulse, with slow release of chromium in the long term.

Ideally treatment of the leachate should reduce the concentration of chromium to that allowed in drinking water (0.10 mg/l) (USEPA, 1974).

When designing a system of fixed bed treatment material to treat the long term leachate of Cr (VI.), the adsorption and desorption properties have to be considered for the various sorbent materials. In this project different materials were studied (charcoal, coir, peat and wood bark) to remove hexavalent chromium from the aqueous phase. Wood bark can reduce aqueous phase Cr (VI) concentration to a non-detectable level. Therefore wood bark could be used as a good sorbent, but other sorbents need to be studied.

In general, potential remediation of the contaminated site is dependent on different factors such as cost effectiveness, public acceptance, and reducing the concentration of chromium to WEL value (Hursthouse, 2001). The cost of different remediation techniques has been reported by USEPA (2000) for in situ treatment of chromium contamination. Actual treatment costs are highly site and application specific and may vary considerably from costs presented on the table below (Table 7-1). Most of those technologies have not gained regulatory acceptance yet and hence need more research and demonstration. Martin and Bardos (1995) reported the range of cost data for different technologies to remediate contaminated soil; such as in situ soil flushing, £25-85/tonne, surface amendments £10-35/tonne, and soil washing £20-160/tonne of soil bulk density of 1800 kg/m^3 (Martin and Bardos, 1995).

Table 7-1 Status of in situ technologies for treatment of chromium contamination.

	Treatment zone	Contaminated media	Status[a]	Treatment cost estimate
Proven technologies				
Geochemical fixation	S,C,D	Groundwater soil	DE, FSA, FTS DE, FTS	$4/m^3$ for saturated zone using ferrous sulphate[b]
Permeable reactive barriers (PRBs) Chemical reduction and fixation (reactive media)	C,D	Groundwater	DE, FSA, FTS	O & M 70-90% less than P & T per year.
Chemical reduction and fixation (ISRM)	C,D	Groundwater	PE, BTS	$3mil/10 yr vs. $9 mil. for P& T
Developing technologies				
Reactive zones Bioreduction (Molasses)	S,C,D	Groundwater	DE, FSA, FTS	$400,000/3 yr vs. $4 mil/20 yr for P&T
Soil flushing/extraction	S,C,D	Groundwater soil	DE, FSA, PE, BTS, DE, FSA	$83 to $237/$m^3$ at assumed soil density of 100 lb/ft[c]
Electro kinetics	S,C	Groundwater soil	DE, FTS, BTS PE, FTS	$25 TO $300/$m^3$ [c]
Emerging technologies				
Phytoremediation	C,D	Groundwater soil	PE, FTS PE, FTS	$18 to 104/$m^3$ at assumed soil density of 100 lb/ft [c]

S=Source zone soil or groundwater, C=Concentrated groundwater plume, D=Diluted groundwater plume, DE=Demonstrated Effectiveness, PE=Potential Effectiveness, FSA=Full scal application, FTS=Field scale Treatability Study, BTS=Bench scale Treatability Study,
a These costs were completed from studies presented in USEPA (2000) document and are for information purposes only.
b Dose not include treatability and design costs, which were significant.
c these cost estimates may not include indirect costs such as permits, treatment of residues, and site preparation.

Recently, various low-cost adsorbents derived from agricultural waste, industrial by-products or natural materials, have been investigated intensively for chromium removal from contaminated wastewater (see Section 6.3). However the expenditure on individual adsorbents varies, depending on the processing employed and its local availability (Sharma, 2003; Kurniawan, et al., 2006). Recently the price of chitosan for removing Cr^{6+}, Hg^{2+}, Cu^{2+}, and Cd^{2+} was reported as $ 16/kg and that of commercial activated carbon

(CAC) is about $ 20- 22/kg depending on its grade and quality. Zeolites have a current price < $1/kg. Lignin is inexpensive, with a price about $ 0.06/kg, and undoubtedly has excellent metal adsorbent binding capacities, which are comparable to that of chitosan, CAC, and other low-cost adsorbents (Babel and Kurniawan, 2003). The process of using low-cost adsorbents seems to be cost effective and may prove useful for large scale treatment of Cr (VI) rich wastewater especially for the developing countries, in contrast with the activated carbon found is more costly and is not affordable for industrial applications (Sharma, 2003; Kurniawan, et al., 2006).

On the basis of the work described in this thesis, various treatment options are suggested.

1. Fe (II) could be used to immobilise chromium at the waste site, which could then be covered by vegetation to limit wind blow. A bed of sorbent could treat chromium leaching to the groundwater. This option would be long-term process.

2. Another possibility could be to mobilise most of the soluble chromium by adding Mn (II) to convert Cr (III) to Cr (VI), which is more mobile. This could be deliberately flushed out of the chromium waste then channelled and leached through a bed of sorbent. Once the initial pulse of chromium has been treated, we could change the bed with the same material or other material for long term slow Cr (VI) leaching.

3. The concept of designing a flow through system requires further studies in order to assess the parameters needed, such as the size of bed and flow rate depending on the chromium concentration and where it could be sited and how often would the bed be changed.

4. One possibility is to treat the restricted bed of sorbent which has high amount of Cr (VI) by adding Fe (II) and adjust the pH to make the perfect condition to reduce Cr (VI) to Cr (III) which is stabilised.

5. The literature is still insufficient to cover this problem and investigations are needed to deal with other locally available and cheap adsorbent materials to eliminate Cr (VI) from industrial wastewater samples with different compositions and characteristics.

6. The mechanisms involved in the immobilisation of Cr on wood bark, as well as any change in the speciation of Cr, will also need to be investigated.

7. · The sorption property of wood bark or any other adsorbent needs more work in terms of the different factors such as, the type and concentration of the adsorbate, contact time, temperature, pH, the surface activation, the surface chemistry of the adsorbent and its aggregation (Markiewicz-Patkowska et al., 2005).

This work attempted to provide suggestions for treatments of waste materials from processing of chromite ore by stabilisation and then treatment of the leachate, or a combination of the two. Chromium contamination is an issue arising in different countries all over the world, such as China, India, and USA (Darrie, 2001) so this suggestion of various treatment options could be applied worldwide on areas which have chromium pollution problems.

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